THERMODYNAMIC PROPERTIES OF HIGH-PRESSURE LIQUID
MIXTURES CONTAINING SUPERCRITICAL COMPONENTS

By

PAUL M. MATHIAS

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1978

TO MY PARENTS

ACKNOWLEDGMENTS

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KEY TO SYMBOLS

A = 2-suffix Margules equation constant

a_i = empirical constants

B_2 = second virial coefficient

B_3 = third virial coefficient

c = microscopic direct correlation function

C = direct correlation function integral

f_i = fugacity of component i

g = radial distribution function

h = (= g-1), total correlation function

H_{ij} = Henry's constant of solute i in pure solvent j

H_{ij} = integrated total correlation function

$\underline{I}$ = identity matrix

K = Boltzmann constant

K_{ij} = binary interaction parameter

n = number of components of mixture

N_i = number of moles of component i in the system

P = pressure

Q = canonical partition function

R = separation between molecules

R = gas constant

$\underline{R}_i$ = position vector of component i

R_m = location of minimum intermolecular potential

t	$=$	dummy variable
T	$=$	absolute temperature
T^*	$=$	characteristic temperature
T_c	$=$	critical temperature
V^*	$=$	characteristic volume
V_c	$=$	critical volume
$\bar{V}_i$	$=$	partial molar volume of component i
$\bar{V}_i^\infty$	$=$	partial molar volume of component i at infinite dilution
V^E	$=$	excess volume of mixing
x_i	$=$	liquid mole fraction of component i
y_i	$=$	vapor mole fraction of component i
y	$=$	$g(r)\ e^{\beta\phi(r)}$

Greek Letters

β	$=$	$1/KT$
γ_i	$=$	total activity coefficient of component i
γ_i^x	$=$	composition activity coefficient of component i
σ	$=$	hard sphere diameter
μ_i	$=$	chemical potential of component i
ϕ	$=$	intermolecular pair potential
ρ	$=$	number density
Ξ	$=$	grand canonical partition function
κ_T	$=$	isothermal compressibility
δ_{ij}	$=$	Kronecker delta

Subscripts

i   = molecule i

ij   = ij pair of molecules

Superscripts

hs   = hard sphere property

r   = reference state

f   = final state

L   = liquid phase

G   = gas phase

MS   = mixed solvent

Underline

—   denotes vector, matrix

Overline

~   denotes reduced quantity

Abstract of Dissertation Presented to the Graduate Council
of the University of Florida in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

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By

Paul M. Mathias

June 1978

Chairman: John P. O'Connell
Major Department: Chemical Engineering

This work is concerned with a method for describing liquid-

phase fugacities in order to predict high-pressure vapor-liquid

equilibrium of systems containing supercritical components.

A solution theory is formulated to provide expressions for

the change in fugacity of components of a multicomponent fluid due

to any change in the state of the system in terms of integrals of

the statistical mechanical direct correlation function. (These

integrals are known to be insensitive to the exact details of the

intermolecular forces for dense fluids and hence a simple empirical

model is proposed to describe them which is based on fluid structure,

but ensures that the numerical calculations are tractable and rapid.

The model has only two parameters for each pure component and a binary

interaction parameter for each pair of components. The results are

relatively insensitive to the value of the latter, thus essentially

predicting the results of mixtures from pure component information.)

Application of the model to pure liquids yields a good equation

of state for liquids, but more importantly provides a means of parameter

determination.

The method provides an excellent description of the nonideality of gas-solvent liquid mixtures including even those with highly polar solvents like water, methanol, ammonia and m-cresol. Therefore, if Henry's constant of the gas and the molar volume and pressure of the solvent are available at any temperature, the method provides good predictions of vapor-liquid equilibrium at elevated pressures.

The method also relates Henry's constants of a solute in two different solvents. Investigations indicate that although these are more sensitive to the binary parameter using the single temperature independent value describes the temperature variation of Henry's constant very well. This method allows for instance a reasonable correlation of methane solubility in n-decane using the methane solubility in water. It is also used to correlate the vapor-liquid equilibrium of hydrogen in various coal oils using the solubility of hydrogen in quinoline. The method also gives good predictions for Henry's constants in mixed solvents except for some aqueous solutions.

All the above results are used to formulate the approach to the general problem, i.e., the arbitrary multicomponent system containing many solutes and solvents. For this purpose at a given temperature the input data required are the molar volumes and vapor pressures of the pure solvents, the matrix of Henry's constants of the solutes in the pure solvents (some of which may be determined as above), and the excess volume of the solute-free solvent mixture. The formulation is tested on the n-butane-n-decane-methane system and the results are quite good when a slight, but reasonable adjustment is made in the solvent volumetric data. This precludes

a definite statement, but overall indications are that the formulation is valid for all multicomponent systems.

Finally, a method is proposed to calculate phase equilibrium by treating the solvent mixture as a pseudo-component. This is very useful for gas solubility in uncharacterized, complex solvent mixtures. Investigations of the n-butane-n-decane-methane ternary indicates that this is likely to be a viable approach.

Design of processing equipment requires reliable phase equilibrium
data. Experimental data are scarce and hence predictions must be made
in many cases. At present, there is no method which can predict high
pressure vapor-liquid equilibrium for systems containing complex
substances, such as water, methanol, and m-Cresol. This work is an
attempt to provide such a method. It requires a small amount of data
as a basis and is applicable to all types of systems containing at
least one supercritical component.

A thermodynamic analysis of multicomponent equilibrium shows
that at equilibrium the fugacity of each component is the same in all
phases. Thus all methods which predict phase equilibrium attempt to
calculate the fugacity in terms of the measurable variables that
characterize the phase. Methods that predict vapor-liquid equilibrium
can, in general, be divided into two categories: those that use the
same model or equation for both phases and those that use separate
equations for each phase.

The first category is best represented by methods that use
empirical equations of state and by corresponding states methods.
Fugacities can be written in terms of Pressure-Volume-Temperature-
Composition (P-V-T-X) relationships of a fluid mixture.[1] Equations
of state provide these relationships and hence the vapor-liquid

equilibrium can be calculated. There have been applications of this approach to mixtures containing nonpolar and slightly polar substances[2,3] which have met with some success. The drawbacks of the method are that the equations of state contain many constants, some of which are temperature dependent, and that the mixing rules for obtaining mixture constants contain some parameters that require binary or higher order data for their evaluation. But if the extensive data required for parameter evaluation is available, equation of state methods can provide reliable estimates of properties for multicomponent systems.

Corresponding states methods are actually a special case of equations of state; this method employs the principle of corresponding states to write properties of a mixture in terms of the properties of a reference fluid. The method can normally characterize substances using fewer parameters than equation-of-state methods as many researchers in the area have shown.[4,5] However, it works well only for mixtures containing substances which are similar to the reference substance.

The dominant weakness of the methods described above is that they attempt to describe the fluid in the two-phase region. The expression for the fugacity of a component involves an integration from zero density to the density of the phase, at constant temperature and composition. Therefore, the integration path for the calculation of liquid-phase fugacities goes through the two-phase region of the fluid. The quantitative description of a fluid in this region is difficult when the fluid contains similar substances; when the substances of the mixture are very different from each other (for example, hydrogen

and decane) this difficulty is greatly increased. Thus it has been proposed that the equation of state description be retained for the vapor phase, but that the liquid phase be described in terms of departures from some conveniently chosen reference state.

In the following discussion we will be quite brief, describing in detail only those aspects where our approach is different from the one conventionally adopted by chemical engineers. (The reader is referred to Prausnitz'[1] book on fluid-phase equilibria for a more complete discussion.) Also, we assume that the vapor-phase properties can be calculated by methods already existing in the literature and confine ourselves to a discussion of the liquid phase.

Adopting the concept of using a liquid reference state we can derive a well-defined thermodynamic expression for the fugacity of any component in a liquid mixture as the product of an ideal value and a factor; the factor, by definition, takes into account deviations from the ideal value. The common practice among chemical engineering thermodynamicists has been to calculate this nonideality factor by invoking a two-step thermodynamic process. Normally this is a change in composition at constant pressure followed by a change in pressure at constant composition, but other variations may be taken. Thus we can write,

$$f_i^L(T,P,\underline{x}) = \left(\frac{f_i}{x_i}\right)^r \left[x_i \left| \gamma_i^x(T,P^r,\underline{x}) \exp\left\{ \int_{P^r}^{P} \frac{\bar{V}_i(T,P,\underline{x})}{RT} \, dP \right\} \right| \right] \qquad (1-1)$$

where the whole quantity in square brackets is the nonideality factor, γ_i^x being the composition correction factor, and the exponential term

(the familiar Poynting correction factor) being the pressure correction factor. Unlike Prausnitz[1] we write the reference quantity explicitly as $(f_i/x_i)^r$. The implications of this are discussed more fully in Chapter 2. Here, it is sufficient to say that this form arises naturally from a fundamental derivation and that it is very flexible. For instance, it goes to the pure liquid fugacity in the case of a pure liquid reference state, and to Henry's constant for a component at infinite dilution. Also, any mixed solvent reference state can be handled without modification.

Equation (1-1) has been shown to be a propitious representation for systems at low pressure where the composition term is dominant. In fact, the work of Prausnitz and coworkers[6] and Fredenslund and coworkers[7] has shown that a large array of liquid nonideality can be predicted to sufficient accuracy using relatively few parameters based on a large data set. However, the situation is different for high pressure systems because the Poynting correction becomes relatively large and must be accounted for accurately. The way some researchers have attacked the problem is by using some correlation to evaluate the Poynting correction and proposing a plausible but essentially empirical model for the composition nonideality. The parameters in the composition nonideality (Gibbs excess free energy) model are then fitted, and subsequently generalized, by using experimental high-pressure vapor-liquid equilibrium data. Prausnitz and Chueh[8] achieved a large degree of success by this approach to nonpolar systems.

Interestingly though, an examination of the actual values of the composition and pressure correction terms shows that for most systems the composition term is less than unity while the pressure correction is greater than unity, and that the total correction is relatively close to unity; sometimes less, but more often greater than unity. For example, in the carbon monoxide-benzene binary the total nonideality correction for carbon monoxide is within a few percent of unity (< 4%) over a large range of liquid conditions in spite of a relatively large Poynting correction (up to 30%). Therefore, from an engineering point of view it seems advantageous to calculate the total change from the same model. To this end we write

$$f_i^L(T,P,\underline{x}) = \left(\frac{f_i}{x_i}\right)^r x_i \gamma_i(T,P,\underline{x};P^r,\underline{x}^r) \tag{1-2}$$

where γ_i (which we call the activity coefficient) is precisely equivalent to the term in square brackets in Equation (1-1). In Equation (1-2) we explicitly indicate that the activity coefficient is a function of the reference state since, of course, it must go to unity at the reference state.

In principle, the quantity γ_i can be calculated by any derivative equation of state.* One particular derivative equation of state is provided by the solution theory of Kirkwood and Buff[9] formulated in

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*By a derivative equation of state we mean an equation or set of equations which provides the partial derivatives of any thermo-dynamic quantity with respect to each of the basis variables.

terms of direct correlation function integrals; here we have the matrix of isothermal partial derivatives of the chemical potential of all components of the system with respect to each of the component number densities. In this work we investigate the value of this theory as a means of predicting deviations from ideality of high-pressure liquid mixtures including those containing components with complex intermolecular forces.

Actually the theory provides a more complete description of liquid mixtures than is implied by Equation (1-2). Consider a binary mixture of a supercritical component S_1 and a subcritical component S_2. The most convenient reference state for this system is pure S_2--the so-called unsymmetric convention. For this system it would seem that the theory does not say anything about $(f_1/x_1)^r$ (= H_{12}, Henry's constant). It turns out however that if we knew Henry's constant of S_1 in any other solvent at the same temperature we could, in principle, calculate H_{12}. In fact, we show that this can be done to sufficient accuracy in many cases (for example, hydrogen in various coal oils). This means that Henry's constant of a solute in any solvent can be considered a "pure component" fugacity since although it is defined with respect to one particular solvent, its value in any other solvent--or solvent mixture for that matter--can be calculated.

Finally, this work represents an attempt to use statistical mechanics to describe the complex systems encountered in chemical processing. Previously, Rogers and Prausnitz[10] have shown that the

Barker and Henderson perturbation theory[11,12] together with the
Kihara model of the intermolecular pair potential can be used to
give good predictions for systems containing essentially spherically
symmetric interactions. Gubbins and coworkers[13] have attempted to
incorporate angle dependent intermolecular forces into their
description of fluid systems and show, using a perturbation theory,
that many curious liquid properties can be predicted. But while
these investigations have produced results of theoretical interest,
they have not been applied practically. This is largely because
of the computer time involved: Rogers and Prausnitz indicate that
it took between 4 and 7 minutes to calculate a typical binary
equilibrium point on a CDC 6600 computer. We have overcome this
difficulty by formulating the problem in terms of quantities that
are known to be insensitive to the exact nature of the intermolecular
forces in a fluid (see Gubbins and O'Connell[14]). Thus, we have
been able to obtain results of practical significance while using
a relatively simple and tractable model.

Chapter 2 contains all the formalism of this work. It begins
with a description of the derivative solution theory for this
particular application and then goes on to show how quantities of
interest can be expressed in terms of direct correlation function
integrals. We also show the many advantages of using temperature
and component number density as the set of thermodynamic basis
variables. In Chapter 3 we describe the model we employ for the
direct correlation function integrals. Chapter 4 discusses the
application of the model to the isothermal compressibility of

pure fluids; this is one means of parameter determination. The
application of the method to high-pressure, binary, gas—solvent
systems is discussed in Chapters 5 and 6.   Finally, in Chapter 7
we propose a general method to predict high-pressure vapor-liquid
equilibrium for multicomponent systems and discuss some of the
problems that arise when there is more than solvent in the system.

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CHAPTER 2
THERMODYNAMICS AND THE DIRECT CORRELATION FUNCTION
SOLUTION THEORY FOR LIQUID PROPERTIES

2.1 Introduction

In the previous chapter we introduced the idea that it might be advantageous to evaluate all deviations from ideality (due to changes in pressure and composition) by a single model. This chapter shows how a solution theory may be employed for this purpose. We develop the formalism which gives the change in the fugacity of any component in the system due to a change in the state of the system. We note some of the desirable features of the representation before going into the details of the derivation.

a. The method employs temperature and component number density as the basis variables. Experience with applied statistical mechanics indicates that this set of variables is of fundamental significance. Also, and perhaps more importantly, the variables are completely independent of each other, simplifying the mathematical manipulation. (Contrast the situation with the use of mole fraction as part of the basis set; in this case the constraint on the sum of the mole fractions makes it impossible to take a partial derivative of any quantity with respect to one mole fraction holding all the other mole fractions constant.)

b.   The formalism expresses quantities of interest in terms
of direct correlation function integrals.   These integrals have been
shown by many authors to be very insensitive to orientation dependent
and nonconformal intermolecular forces in a fluid in the dense fluid
region.   Gubbins and O'Connell[1] have shown that if the temperature
and density are suitably reduced the direct correlation function
integrals of substances as different as Argon and water can be
superimposed.   Brelvi and O'Connell[2,3] have demonstrated that in
the liquid region the direct correlation function integrals of a
wide variety of substances are insensitive to temperature and may
be correlated on the basis of a size parameter only.   Thus, it seems
likely that a relatively simple model for the direct correlation
function integrals will yield an accurate description of real systems.

Section 2 describes the solution theory and the quantities
involved.   Section 3 derives thermodynamic equations for calculating the
nonideality of general multicomponent systems.   Finally, in Section 4
we discuss some ramifications of taking the approach.

2.2   Statistical Thermodynamic Formalism.   Derivation and Discussion of Fundamental Equations

This section shows how density fluctuations in open systems
may be used to derive expressions for fluctuation quantities in terms
of direct correlation function integrals.   The major content of this
section has been reported previously[4,5] but we repeat it in order
to emphasize some points of interest.

Consider an open, homogeneous, n-component system defined
by the variables temperature, chemical potential of the n components,
and total volume ($T,\underline{\mu},V$; throughout this report we denote vectors

by an underline). We define a singlet number density $\rho_i^{(1)}(\underline{R}_1)$ as

the time-averaged density of molecular centers of type i at the

position $\underline{R}_1$. Note that the density is averaged over all orienta-

tions in the case of structured particles since we only consider

the location of the center of the molecule. In similar fashion

we define the pair number density $\rho_{ij}^{(2)}(\underline{R}_1,\underline{R}_2)$ as the average

density of molecular pairs of type i at position $\underline{R}_1$ and type j at

$\underline{R}_2$. Integration of $\rho_i^{(1)}(\underline{R}_1)$ and $\rho_{ij}^{(2)}(\underline{R}_1,\underline{R}_2)$ over the volume of the

system gives, by definition, the time-averaged number of particles

and the time-averaged number of i-j pairs in the system. Therefore,

$$\int^V \rho_i^{(1)}(\underline{R}_1)\ d\underline{R}_1 = <N_i> \tag{2-1}$$

$$\iint^{V\ V} \rho_{ij}^{(2)}(\underline{R}_1,\underline{R}_2)\ d\underline{R}_1 d\underline{R}_2 = <N_i N_j> - \delta_{ij}<N_i> \tag{2-2}$$

where the usual notation has been used for a time-averaged quantity

and δ_{ij} is the Kronecker delta.

A useful quantity that gives an indication of the interaction

between the particles of the system is the pair correlation function

or the radial distribution function. It is defined as,

$$g_{ij}^{(2)}(\underline{R}_1,\underline{R}_2) = \frac{\rho_{ij}^{(2)}(\underline{R}_1,\underline{R}_2)}{\rho_i^{(1)}(\underline{R}_1)\ \rho_j^{(1)}(\underline{R}_2)} \tag{2-3}$$

This function can very easily be shown to be the normalized conditional

probability of finding particle j at $\underline{R}_2$ given that particle i is at $\underline{R}_1$.

In a homogeneous system $\rho_i^{(1)}(\underline{R}_1)$ is independent of the position $\underline{R}_1$ and is equal to the average number density of species i. Hence, from here on we simply refer to the quantity as ρ_i. Also, the pair correlation function depends only on the scalar distance R ($= |\underline{R}_1 - \underline{R}_2|$) between $\underline{R}_1$ and $\underline{R}_2$. Thus we can write,

$$\frac{1}{V} \int (g_{ij}^{(2)}(R)-1)d\underline{R} = \frac{<N_iN_j> - <N_i><N_j>}{<N_i><N_j>} - \frac{\delta_{ij}}{<N_i>} \qquad (2-4)$$

The notation of the radial distribution function in Equation (2-4) has been simplified; $g_{ij}^{(2)}(R)$ gives the normalized probability of finding a particle of type j at a distance R from a particle of type i. We also note that Equation (2-4) gives an indication of the interaction of the particles of the system. If there is no interaction, then

$$<N_iN_j> = <N_i><N_j>$$

and the right hand side of Equation (2-4) is zero except for a negligible contribution from the second term when i = j. In this case $g_{ij}(R) = 1$. However, in all cases of interest the interaction between particles is significant. It has been usual to approximate the total interaction energy between particles as the sum of inter- actions of all molecular pairs. This pair interaction is dependent only on the relative separation, and possibly orientation, of the molecules of the pair. Figure (2-1) shows the quantitative form of a spherically symmetric pair potential and of the resulting
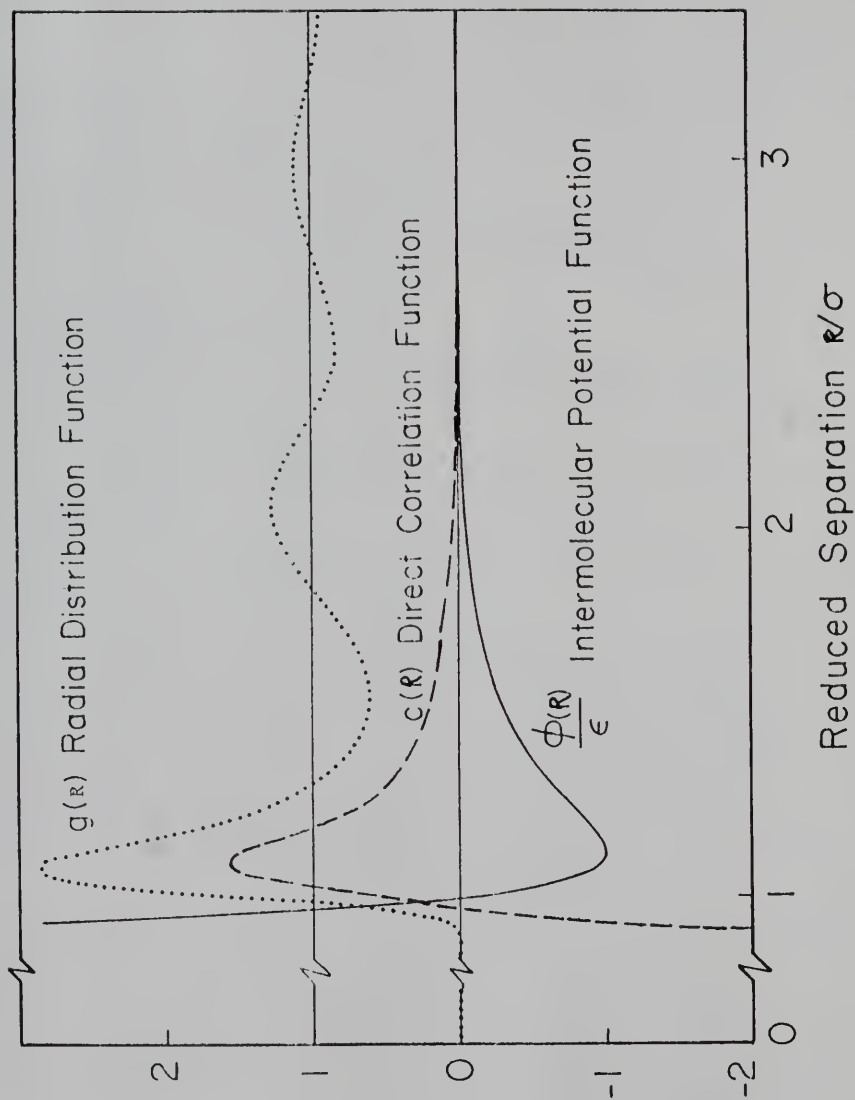
Figure 2-1. Molecular correlation functions for liquids

radial distribution function. We do not explicitly consider a pair potential in this work--and in fact the equations derived in this chapter are independent of any assumptions like pairwise additivity-- but it is useful to visualize properties as resulting from interactions of this form.

An equation similar to Equation (2-4) but containing thermo-dynamic variables can be derived from statistical mechanics. Consider the statistical mechanical construct of the grand canonical ensemble[6] (precisely the same as the open system we have already defined). We can write the probability that the n-component system will contain $N_1, N_2 \ldots N_n$ molecules of the n species as

$$P(N_1, N_2, \ldots N_n) = \frac{e^{\frac{1}{KT} \sum_{i=1} N_i \mu_i} Q(T, V, N_1, \ldots N_n)}{\Xi} \qquad (2-5)$$

where Q and Ξ are the canonical and grand canonical partition functions defined by

$$Q = \int \cdots \int e^{-H/KT} \, dp^N dq^N$$

$$\Xi = \sum_{N_1, N_2, \ldots N_n} e^{-\frac{1}{KT} \sum N_i \mu_i} Q(T, V, N_1, \ldots N_n) \qquad (2-6)$$

From the probability expressions the average number of particles and particle pairs can be written as

$$\langle N_i \rangle = \sum_{N_1, N_2, \ldots N_n} N_i \, P(N_1, \ldots N_n)$$

$$= \frac{KT}{\Xi} \left(\frac{\partial \Xi}{\partial \mu_i} \right)_{T, V, N_{j \neq i}} \tag{2-7}$$

$$\langle N_i N_j \rangle = \sum_{N_1, N_2, \ldots N_n} N_i N_j \, P(N_1, \ldots N_n)$$

$$= \frac{(KT)^2}{\Xi} \frac{\partial^2 \Xi}{\partial \mu_i \, \partial \mu_j}$$

$$= \frac{(KT)^2}{\Xi} \frac{\partial (\langle N_i \rangle \, \Xi / KT)}{\partial \mu_j}$$

$$= \langle N_i \rangle \langle N_j \rangle + \left(\frac{\partial \langle N_i \rangle}{\partial \mu_j / KT} \right)_{T, V, \mu_{k \neq j}} \tag{2-8}$$

From Equations (2-4) and (2-8) we get

$$\frac{1}{\langle N_i \rangle} \left(\frac{\partial \langle N_i \rangle}{\partial \mu_j / KT} \right)_{T, V, \mu_{k \neq j}} = \rho_j \int (g_{ij}^{(2)}(R) - 1) d\underline{R} + \delta_{ij} \tag{2-9}$$

Since V is held constant we can write the above equation as

$$\frac{1}{\rho} \left(\frac{\partial \rho_i}{\partial \mu_j / KT} \right)_{T, V, \mu_{k \neq j}} = x_i x_j \, \rho \int (g_{ij}^{(2)}(R) - 1) d\underline{R} + x_i \delta_{ij} \tag{2-10}$$

Equation (2-10) is the basic equation of the Kirkwood-Buff solution theory.[4] A few authors[7,8] have attempted to apply this equation by employing elementary thermodynamic relations to express

composition derivatives of the chemical potential at constant temperature and pressure in terms of functions involving integrals over the radial distribution function. This approach has led to enormous equations of intractable complexity and very few practical results. Further, since the radial distribution function is generally a long ranged correlation, integrals of the form of (2-4), (2-9) and (2-10) diverge at the critical point. Therefore, it would be desirable to express Equation (2-10) in terms of some function which is the inverse of the radial distribution function (or matrix inverse in the case of multicomponent systems) and yet obtain a simple tractable result. Fortunately this can be accomplished by defining a function called the pair direct correlation function, $c(r)$.

$$g_{ij}^{(2)}(\underline{0},\underline{R}) - 1 \equiv c_{ij}^{(2)}(\underline{0},\underline{R}) + \sum_k \rho_k \int c_{ik}^{(2)}(\underline{0},\underline{R}_1) \ [g_{ij}^{(2)}(\underline{R},\underline{R}_1) - 1]d\underline{R}_1$$

(2-11)

The function we have defined is very similar to the one defined by Ornstein and Zernike.[9] The only difference between the two is that we use the angle averaged radial distribution whereas the original definition contains the actual, orientation dependent quantity; of course, in the limiting case of a fluid with spherically symmetric interactions the two definitions are identical. However, previous results[1,2] indicate that integration of Equation (2-11) over $\underline{R}$ yields the same results as integrating the original equation over orientation and separation. Apparently in dense fluids, the angular indirect correlations (contributions from the integral in Equation (2-11)) are unimportant and the integrals over the second term on

the right hand side are separable. We reiterate here that this whole
work is based on this rather surprising result. Thus, from this point
on we assume that all contributions from particle correlations can be
modelled as arising from spherically symmetric interactions.

The qualitative form of the direct correlation function is
shown in Figure 2-1. It is quite difficult to give a physical
interpretation to this correlation function (see Percus[10] for an
indepth discussion). For the purposes of this chapter we assume
that this function is one whose integral is easily modellable.
Thus, any approach which expresses quantities of interest in terms
of direct correlation function integrals could be implemented
practically.

We now go back to the derivation at hand. Integrating
Equation (2-11) over all $\underline{R}$ gives

$$\rho \int (g_{ij}^{(2)}(\underline{0},\underline{R})-1)dR = \rho \int C_{ij}^{(2)}(\underline{0},\underline{R})d\underline{R} + \sum_k x_k \left| \rho \int C_{ik}^{(2)}(\underline{0},\underline{R})d\underline{R} \right| \times$$

$$\left| \rho \int (g_{kj}^{(2)}(\underline{0},\underline{R}_1)-1)dR_1 \right|$$

$$H_{ij} = C_{ij} + \sum_k C_{ik}x_k H_{kj} \qquad (2-12)$$

where H_{ij} and C_{ij} are the integrals over the total correlation func-
tion $(g_{ij}^{(2)}(R)-1)$ and the direct correlation function respectively.

In matrix notation Equation (2-12) can be written as

$$\underline{H} = \underline{C} + \underline{C} \, \underline{X} \, \underline{H} \qquad (2-13)$$

where $\underline{H}$ and $\underline{C}$ are the matrices whose elements are H_{ij} and C_{ij} respectively, and $\underline{X}$ is a diagonal matrix with X_{ii} equal to the mole fraction of the ith component, x_i. Equation (2-13) can be written as

$$\underline{I} + \underline{H}\,\underline{X} = (\underline{I} - \underline{C}\,\underline{X})^{-1} \tag{2-14}$$

Equation (2-10) can also be written in matrix notation as

$$\underline{X}(\underline{I} + \underline{H}\,\underline{C}) = \underline{A} \qquad \text{where} \quad A_{ij} = \frac{1}{\rho}\left(\frac{\partial \rho_i}{\partial \mu_j/KT}\right)_{T,V,\mu_{k \neq j}} \tag{2-15}$$

Equations (2-14) and (2-15) can be combined to give

$$(\underline{I} - \underline{C}\,\underline{X})\underline{X}^{-1} = \underline{A}^{-1} \tag{2-16}$$

where

$$(A^{-1})_{ij} = \rho\left(\frac{\partial \mu_i/KT}{\partial \rho_j}\right)_{T,\rho_{k \neq j}} \tag{2-17}$$

and therefore the individual elements of Equation (2-16) are

$$\left(\frac{\partial \mu_i/KT}{\partial \rho_j}\right)_{T,\rho_{k \neq j}} = \frac{\delta_{ij}}{\rho_i} - \frac{C_{ij}}{\rho} \tag{2-18}$$

For any isothermal change, the Gibbs-Duhem equation is

$$dP = \sum \rho_i\, d\mu_i$$

Therefore, we can write

$$\left(\frac{\partial P/KT}{\partial \rho_i}\right)_{T,\rho_{j\neq i}} = 1 - \sum_j x_j C_{ij} \qquad (2-19)$$

Equations (2-18) and (2-19) are the only two basic equations that we use. In the next section we show that a simple thermodynamic approach can be used to calculate the change in properties of a system due to an isothermal change in the measurable variables.

2.3 Derivation of Thermodynamic Equations

If any theory is to be applied in practical situations, it must express properties of interest in terms of convenient measurable variables. For the description of chemical processes these convenient variables are temperature, pressure, and mole fraction of the components of the system. But Equations (2-18) and (2-19) are most easily used if the system is described in terms of temperature, and number density of the n components. Also, from the point of view of a model for the direct correlation function integrals (Chapter 3), the most appropriate set of variables is temperature and component number density. The way we reconcile these two requirements is to use the theory to calculate the change in component number density due to a change in pressure and composition, then changes in other thermodynamic properties are calculated.

Some authors[11] have attempted to use the equations of the type derived in the previous section by writing infinite series expansions (involving higher order correlation functions) about a reference point in the solution. Here, our approach is different. We assume that we have available a method of calculating the second

order correlation functions for all conditions of the fluid. Thus we obtain expressions which do not involve correlation functions other than second order.

Consider a n-component, homogeneous fluid in an arbitrary reference state characterized by temperature, pressure, mole fraction of the n components, and specific volume (note that the system is overspecified since, according to the phase rule, it has only n+1 degrees of freedom). We now wish to use the equation developed in the previous section to calculate the change in properties when the fluid state is changed isothermally to some other pressure and composition. Let us denote reference state and final state properties by the superscripts 'r' and 'f' respectively. Define a dummy variable t such that for all components

$$\rho_i(t) = \rho_i^r + (\rho_i^f - \rho_i^r)t \qquad i=1,\ldots n \qquad (2\text{-}20)$$

The variable t operates in a similar fashion to the extent of reaction used in the thermodynamics of reaction equilibria.

We can now evaluate the change in any thermodynamic quantity Q, a function of $T, \underline{\rho}$, due to a change in the system from the initial to the final state as a change due to variable t changing from 0 to 1. Thus,

$$Q^f - Q^r = \int_0^1 \frac{dQ}{dt}\, dt$$

$$= \int_0^1 \left\{ \sum_{i=1} \left(\frac{\partial Q}{\partial \rho_i}\right)_{T,\rho_{j\neq i}} \frac{\partial \rho_i(t)}{\partial t} \right\} dt$$

$$= \sum_{i=1}^{n} (\rho_i^f - \rho_i^r) \int_0^1 \left(\frac{\partial Q}{\partial \rho_i}\right)_{T,\rho_{j\neq i}} dt \qquad (2-21)$$

Therefore for the change in pressure we get,

$$\frac{P^f - P^r}{RT} = \sum_{i=1}^{n} (\rho_i^f - \rho_i^r) \left\{ 1 - \int_0^1 \left| \sum_{j=1}^{n} x_j C_{ij}(T,\underline{\rho}(t)) \right| dt \right\} \qquad (2-22)$$

Note here that we have changed over from a molecular to a molar representation thus replacing K by R. We use the same symbol for molecular and molar density since this causes little or no confusion.

In practice it is easier to deal with the fugacity than with the chemical potential.[12] Thus we rewrite Equation (2-18) as

$$\left(\frac{\partial \ell n f_i}{\partial \rho_j}\right)_{T,\rho_{K\neq j}} = \frac{\delta_{ij}}{\rho_i} - \frac{C_{ij}}{\rho} \qquad (2-23)$$

From Equations (2-21) and (2-23) we get

$$\ell n\, f_i^f - \ell n\, f_i^r = \ell n\, \frac{\rho_i^f}{\rho_i^r} - \int_0^1 \left| \sum_{j} (\rho_j^f - \rho_j^r) \frac{C_{ij}(T,\underline{\rho}(t))}{\rho(t)} \right| dt \qquad (2-24)$$

Therefore,

$$\ln\ f_i^f = \ln\left(\frac{f_i^r}{x_i^r}\right) + \ln\ x_i^f + \ln\ \frac{\rho^f}{\rho^r} - \int_0^1 \left[\sum_j\ (\rho_j^f - \rho_j^r)\ \frac{C_{ij}(T,\underline{\rho}(t))}{\rho(t)}\right] \quad (2\text{-}25)$$

Equation (2-25) is precisely in the form of Equation (1-2). Now if a problem is formulated in terms of T-P-x, it is easy to see that Equation (2-22) can be used to solve iteratively for the final total density and then Equation (2-25) can be used to calculate the change in fugacity of all components. Appendix C describes the numerical method we have developed to implement the procedure.

2.4 Discussion

The above development shows that if direct correlation function integrals can be predicted reliably as a function of temperature and component number density, deviations from ideality can be accurately calculated. However, this method is new and thus will be unfamiliar to most readers. Therefore in this section we discuss some of the features of the approach.

First, Figure 2-2 is a qualitative representation of our approach to the calculation of the activity coefficient of a component in a binary mixture. Here, the reference state has arbitrarily been chosen as pure 2. The integration path we have adopted is a straight line in the $\rho_1 - \rho_2$ plane connecting the initial and final states. For comparison we also show the integration path corresponding to a method conventionally used. We note here that the calculation does not increase in complexity as the number of components in the system increase. We also note that although Equations (2-22) and (2-25) may look formidable actual
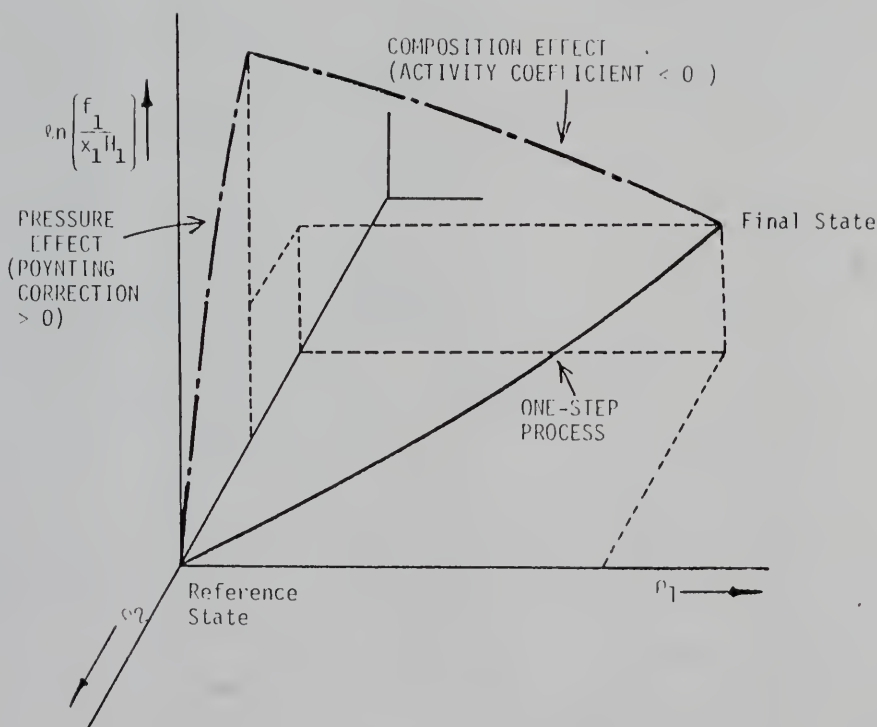
Figure 2-2. Schematic representation of the calculation
of the activity coefficient and comparison
with conventional calculation

calculations are easy to perform. The solution procedure we have adopted is stable and quite fast; on the average it takes about one-tenth of a second to calculate a typical binary equilibrium point on the Amdahl computer at the University of Florida.

Second, we note that the equations are simple in form and independent of the reference state chosen. For a pure component reference state f_i^r/x_i^r is $f_i^{L\ pure}(T^r, P^r)$; for infinite dilution the quantity f_i^r/x_i^r becomes Henry's constant. Further, the model and equations are precisely of the same form for any reference state. Recall that for methods involving the Gibbs excess free energy different models are required--or perhaps more accurately, the same model must be normalized differently. Probably of most value, the representation of infinite dilution of a component in a mixed solvent does not pose any problems; in fact, as we show below, it provides some useful requirements on the parameters.

Third, since the model provides a complete description of any change of state of a system, there can be only one reference state for all components. Any other reference state will be either redundant or inconsistent. If the system consists of many super-critical species and one subcritical substance, then the most convenient (unique) reference state is the pure saturated sub-critical, i.e., all the supercritical species at infinite dilution in the subcritical specie. For this system the above development can be used in a straightforward manner to calculate properties of interest. But now consider the case of two subcritical (solvent)

substances in the system. Here we would have information about both
of the states containing pure solvents. But the model can be used
to calculate the properties in one solvent from those in the other.
Thus, as stated earlier, the properties in the second solvent are
either redundant or inconsistent. We show in later chapters that
the inconsistency can be used for parameter determination; in any
case this inconsistency must be removed.

Further, consider a system with a supercritical substance S_1
and two subcritical substances, S_2 and S_3. As we have shown, the model
can be used to calculate the ratio of Henry's constants of S_1 in pure
S_2, H_{12} and of S_1 in pure S_3, H_{13} by going from pure S_2 as the initial
state to pure S_3 as the final state. In similar fashion we can calculate
the same ratio by taking the reverse path. Now, because of the nonexact
nature of the model, if the final state is specified in terms of pressure,
these ratios will not be equal and the innate symmetry of the system will
be lost. However, if the final state is specified in terms of total
number density the symmetry will be retained since the two ratios will
always be equal. The symmetry requirement is more than an esthetic
consideration. This is shown by adding another subcritical substance
S_4 to the system. Now we can show that if we have good predictions for
the ratios involving solvents S_2 and S_3, and for S_2 and S_4, then the
symmetry insures that we have a good prediction for the ratio involving
S_3 and S_4. More importantly, we can now predict Henry's constant of
S_1 in the mixed solvent; here, of course, we would require the mixed
solvent density, or, in more familiar terms, the excess volume of mixing
of the mixed solvent state.

A final point we wish to make is that although solvent-solvent nonidealities can, in principle, be predicted from the model, a severe small-difference-of-large-numbers problem is encountered and thus the prediction is very unreliable. Therefore, in the implementation of the approach on a general n-component system while we use the theory to calculate the reference state (solute-free mixed solvent) fugacities of the supercritical components, the reference state fugacities of the solvents are assumed to be input data. We expect however that solvent reference fugacities will be calculable by already existing methods.[12]

Most of the considerations in this chapter will be pursued in greater depth in later chapters. The discussion given here should only be considered a preview.

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CHAPTER 3
TWO-PARAMETER MODEL FOR DIRECT CORRELATION
FUNCTION INTEGRALS IN LIQUIDS

This chapter describes the model we have developed to describe all the pair direct correlation function integrals of a multicomponent liquid. The parameters required are a characteristic temperature T^* and a characteristic volume V^* for each component of the system and a binary interaction parameter for all unlike pairs. Section 3.1 describes the pure fluid model and Section 3.2 shows how the pure fluid model is extended to mixtures.

3.1 Pure Fluid Model

Three considerations went into the choice of the model for the pure fluid direct correlation function integrals:

i) The works of Gubbins and O'Connell,[1] and Brelvi and O'Connell[2,3] have shown that this quantity can be modeled easily. Thus, we expect that some form of two-parameter corresponding states theory would provide an adequate description.

ii) Fundamental statistical mechanics research on perturbation theories[4-6] has shown that in the dense liquid region correlation functions are predominantly determined by repulsive forces. These in turn can be approximated as hard sphere interactions with a condition dependent hard sphere size.

iii) We would like to have a pure fluid representation which allows easy extension to the mixture case.

For a pure fluid, Equation (2-19) becomes

$$1-C = \left(\frac{\partial P/RT}{\partial \rho}\right)_T = \frac{1}{\rho K_T RT} \text{ - reduced isothermal compressibility} \tag{3-1}$$

Also for the virial expansion for the compressibility factor we obtain

$$\left(\frac{\partial P/RT}{\partial \rho}\right)_T = 1 + 2B_2\rho + 3B_3\rho^2 + \ldots \tag{3-2}$$

where B_2 is the second virial coefficient, B_3 is the third virial coefficient and so on.

We now propose that an expression for the pure fluid direct correlation function integrals which is consistent with the above considerations is

$$1-C = 1-C^{hs} + 2\rho(B_2 - B_2^{hs}) \tag{3-3}$$

where C^{hs} is the direct correlation function of a hard sphere fluid and B_2^{hs} is the second virial coefficient of the hard sphere fluid. (This form of expression has been used before.[7])

Equation (3-3) is in qualitative agreement with consideration (ii) since at high density the dominant contribution to C will be from C^{hs}. We have replaced the hard sphere second virial coefficient

by the actual second virial coefficient since at normal conditions
the second virial coefficient is negative, i.e., the attractive
forces outweigh the repulsive forces. This can be considered a way
of accounting for the attractive forces.

Equation (3-3) also satisfies consideration (iii) since it
can very easily be generalized to mixtures. The Carnahan-Starling
equation[8,9] provides an accurate estimate of direct correlation
function integrals in hard sphere mixtures. The second virial
coefficient is a two-body term and hence is the same, in principle,
in the mixture as in the pure fluid. Of course, some method must be
used to calculate the cross second virial coefficients.

We now assert that consideration (i) justifies a postulate
that :

a. The reduced hard sphere diameter is some universal
function of reduced temperature and reduced density, and

b. The reduced second virial coefficient is some universal
function of reduced temperature.
In other words, if we can find empirical correlations for the reduced
hard sphere diameter and the reduced second virial coefficient for
some reference fluid, they will have universal validity. We chose
Argon (and Krypton and Xenon suitably reduced[10,11]) as the reference
substance since a large amount of reliable data are available.[12-17,22-23]
For this substance we fixed the characteristic parameters as the
corresponding critical constants.

The correlation for the reduced second virial coefficient was adapted from that presented by Tsonopoulos[18] (Tsonopoulos uses a characteristic temperature and a characteristic pressure whereas we use a characteristic temperature and a characteristic volume; the change however is simple, requiring only that all parameters be multiplied by a constant). The correlation is shown in Table 3-1, Equation (3-4). For the direct correlation function of the hard sphere fluid we use the Carnahan-Starling equation.[8,9] Now at each point for which data was available we found the hard sphere diameter which matched the calculated reduced isothermal compressibility with the experimental value. The reduced hard sphere diameters obtained are shown in Figure 3-1. From the form of the curves we deduced an empirical correlation and the constants of the correlation were fitted by a least-squares technique. The rather complicated function is shown in Table 3-1. The particular form was chosen because it has the following features:

a) At high reduced temperatures the hard sphere diameter is a function of reduced temperature only as might be expected.

b) At high densities the hard sphere diameter is a function of temperature only. This again is to be expected since a hard sphere fluid is a good model of a fluid at high density.

c) The first two exponential terms were chosen to represent the minimum in the isothermal change of the hard sphere diameter with density. The particular form was chosen since the position of the minimum seemed to shift somewhat linearly with temperature.

d) The last exponential term is used for changes in the hard sphere diameter required to obtain an accurate representation
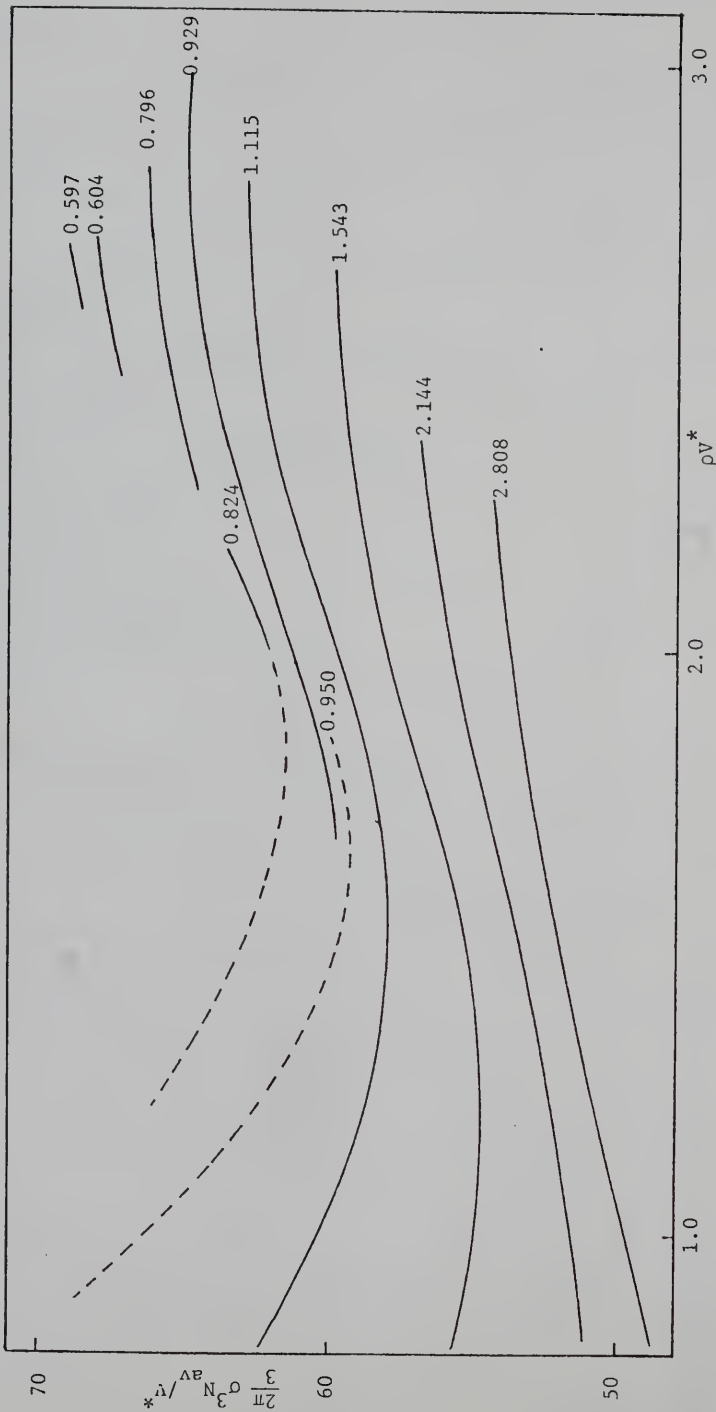
Figure 3-1. Experimental variation of reduced hard sphere diameter. The numbers on the figure refer to reduced temperature (T/T*) isotherms

Table 3-1

Universal Correlations for the Reduced Second Virial
Coefficient and the Reduced Hard Sphere Diameter[*]

Reduced Temperature: $\tilde{T} = T/T^*$

Reduced Density: $\tilde{\rho} = \rho \, V^*$

a. Reduced Second Virial Coefficient

$\tilde{T} \leq 3.2$: $\dfrac{B_2}{V^*} = 0.4966 - \dfrac{1.134}{\tilde{T}} - \dfrac{0.4759}{\tilde{T}^2} - \dfrac{0.0416}{\tilde{T}^3} - \dfrac{0.00209}{\tilde{T}^8}$ (3-4)

$\tilde{T} \geq 3.2$: $\dfrac{B_2}{V^*} = 0.3301 - \dfrac{0.1376}{\tilde{T}} - \dfrac{1.972}{\tilde{T}^2}$ (3-5)

b. Reduced Hard Sphere Diameter

$\tilde{T} \geq 0.73$: $f_s = a_7/\tilde{T}^{a_8}$

(3-6)

$\tilde{T} \leq 0.73$: $f_s = a_{14} \exp[- a_{15}\tilde{T}]$

$\dfrac{\frac{2\pi}{3} N_{av}\sigma^3}{V^*} = f_s + a_2/\exp[a_4(\tilde{\rho} + a_1\tilde{T})^2] - a_3/\exp[a_5(\tilde{\rho} + a_1\tilde{T} - a_6)^2]$

$+ a_9/\exp[a_{10}\{(\tilde{T} - a_{13})^2 + a_{11}(\tilde{\rho} - a_{12})^2\}]$ (3-7)

$a_1 = 0.54008832$ $a_8 = 0.17565885$

$a_2 = 1.2669802$ $a_9 = 0.18874824$

$a_3 = 0.05132355$ $a_{10} = 17.952388$

$a_4 = 2.9107424$ $a_{11} = 0.48197123$

$a_5 = 2.5167259$ $a_{12} = 0.76696099$ $a_{13} = 0.76631363$

$a_6 = 2.1595955$ $a_{14} = 0.809657804$

$a_7 = 0.64269552$ $a_{15} = 0.24062863$

[*]Note that correlation is completely in terms of reduced variables
and thus the constants are independent of the particular units chosen
for V^* and T^*.

in the critical region. It is somewhat surprising to us that
constants a_{12} and a_{13} are not closer to unity.

The functional form of the high density asymptote of the
reduced hard sphere diameter (f_s in Equation (3-6)) must be chosen
with care since argon data is available only over a limited tempera-
ture range ($\tilde{T} = 0.6 - \tilde{T} = 2.8$) and yet many fluids of practical
interest are normally at reduced temperatures outside the range.
A plot of this asymptote (estimated from Figure 3-1) against reduced
temperature indicates that the logarithm of the high density asymptote
curves linearly with the logarithm of the reduced temperature. Thus,

$$\ln f_s \approx \ln a_7 - a_8 \ln \tilde{T} \tag{3-8}$$

We chose the functional form of Equation (3-6) by using Equation
(3-8) and by making our function qualitatively consistent with the
Barker and Henderson perturbation theory.[20] In order to use the
results of this theory we have to define an intermolecular pair poten-
tial, but, for our purposes, the definition does not have to be quan-
titative and we need only assume that the pair potential has the
qualitative form shown in Figure 2-1. The Barker-Henderson hard
diameter is given by

$$\frac{\sigma_{BH}}{r_o} = \int_0^1 \left\{ 1 - \exp\left|\frac{\overline{\phi(z)}}{\underline{KT}}\right| \right\} dz \tag{3-9}$$

where σ_{BH} is the Barker-Henderson hard sphere diameter, r_o is an
intermolecular separation which represents the repulsive interaction

between the molecules (Barker and Henderson somewhat arbitrarily assume r_o is the intermolecular separation corresponding to the zero of the pair potential), and z $(= \mathcal{R}/r_o)$ is the reduced separation.

An extrapolation of Equation (3-8) into the high temperature region is in qualitative agreement with Equation (3-9) since Equation (3-9) indicates that the hard sphere diameter decreases with increasing temperature, but the effect of an increase in temperature decreases with increasing temperature since the pair potential becomes very steep at small separations.

Equation (3-8) predicts that the asymptote increases without limit as the temperature decreases. But this is clearly in disagreement with Equation (3-9) which indicates that the hard sphere diameter approaches a constant value of r_o at low temperatures. Thus we assume that at low temperatures the asymptote has the essentially empirical but qualitatively correct form,

$$f_s = a_{14} \exp\,[-\,a_{15}\tilde{T}] \tag{3-11}$$

and we insist that the two functional forms have the same value and first derivative at some change-over temperature $\tilde{T}_o$. This gives the following relations between the constants in Equations (3-8) and (3-11):

$$a_{14} = \frac{a_7}{\tilde{T}_o^{a_8}} \exp\,(a_8) \tag{3-12}$$

$$a_{15} = a_8/\tilde{T}_o \tag{3-13}$$

The complete functional form was fitted to compression data by a least-squares technique. The values of the constants obtained are shown in Table 3-1, and the high density asymptote of the reduced hard sphere diameter is plotted in Figure 3-2. We note that the low temperature asymptote of the hard sphere fluid for argon corresponds to a hard sphere diameter of 3.65Å. An accurate evaluation of the argon pair potential[21] indicates that the zero and minimum of the potential correspond to separations of 3.4Å and 3.8Å respectively. Thus, our reasoning seems qualitatively correct. However, we would not recommend the use of this correlation at temperatures below $\tilde{T} = 0.38$.

The representation should be valid for supercritical substances which are at very high reduced temperatures; for example, the reduced temperature of hydrogen at room temperature is about 8. Although, as discussed above, the reduced hard sphere diameter correlation should be valid at these high reduced temperatures, the second virial coefficient of Tsonopoulos[18] is not applicable. Hence, we adapted a correlation of Deming and Shupe[19] for hydrogen and pieced the two correlations together at the "glueing point", $\tilde{T} = 3.2$. The high temperature form is shown in Equation (3-5). Table 3-2 shows the value of the reduced second virial coefficient and its temperature derivative for the complete correlation.

Table 3-3 shows the prediction of the reduced isothermal compressibility (1-C) for a wide range of reduced conditions. The representation calculates the change in pressure corresponding to a change in density to an average accuracy of 0.61% for argon.
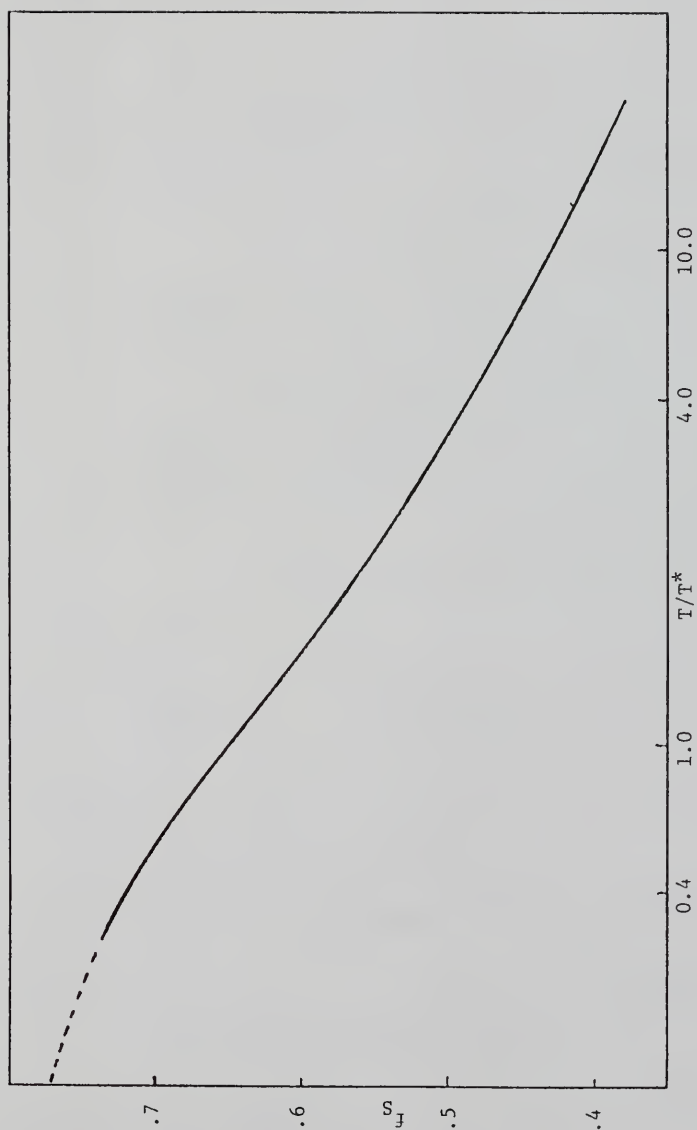
Figure 3-2. Variation of the asymptote of the reduced hard sphere diameter with reduced temperature

Table 3-2

Reduced Second Virial Coefficient and Its
Temperature Derivative

$$\tilde{T} = T/\tilde{T}$$

$$\tilde{B}_2 = B_2/V^*$$

$\tilde{T}$	$\tilde{B}_2$	$\dfrac{d\tilde{B}_2}{d\ 1/\tilde{T}}$
0.35	$-\ 16.88$	$-\ 30.86$
0.4	$-\ 9.15$	$-\ 14.50$
0.5	$-\ 4.54$	$-\ 5.68$
0.6	$-\ 3.03$	$-\ 3.66$
0.7	$-\ 2.25$	$-\ 2.95$
0.8	$-\ 1.76$	$-\ 2.60$
0.9	$-\ 1.41$	$-\ 2.38$
1.0	$-\ 1.16$	$-\ 2.23$
1.5	$-\ 0.483$	$-\ 1.82$
2.0	$-\ 0.195$	$-\ 1.64$
3.2^-	$+\ 0.095$	$-\ 1.44$
3.2^+	$+\ 0.095$	$-\ 1.37$
5.0	0.224	$-\ 0.93$
10.0	0.297	$-\ 0.53$
20.0	0.319	$-\ 0.33$

Table 3-3

Prediction of Reduced Isothermal Compressibility (1-C) as a Function of Reduced Temperature and Density

$\rho V^* / \Gamma T^*$	0.400	0.600	0.800	1.000	1.500	2.000	5.000	20.000
0.20	- 2.456	- 0.069	0.396	0.606	0.842	0.949	1.107	1.139
0.40	- 5.774	- 1.026	- 0.105	0.285	0.744	0.951	1.256	1.302
0.60	- 9.133	- 1.864	- 0.390	0.081	0.715	1.009	1.457	1.494
0.80	-12.406	- 2.496	- 0.383	0.035	0.764	1.127	1.719	1.719
1.00	-15.475	- 3.147	- 0.585	0.012	0.892	1.322	2.053	1.982
1.20	-18.269	- 3.811	- 0.994	- 0.004	1.123	1.646	2.474	2.289
1.40	-20.734	- 4.185	- 1.111	0.161	1.532	2.181	3.001	2.646
1.80	-24.415	- 3.611	0.061	1.655	3.443	4.217	4.470	3.548
2.20	-23.607	1.090	4.956	6.455	7.744	7.900	6.723	4.772
2.60	- 9.549	15.884	17.385	17.023	15.428	14.047	10.177	6.438
3.00	33.474	49.812	42.793	37.175	29.055	24.663	15.517	8.719
3.40	146.711	127.235	96.551	77.798	54.631	43.664	23.907	11.867
3.80	484.690	328.374	223.240	167.262	105.427	79.143	37.392	16.255

Application to other substances is described in Chapter 4. The regions

of negative compressibility--corresponding to mechanical instability--

are all in the two-phase region except for the negative values in the

critical isotherm. Thus the representation does not predict the

critical point exactly. But this is not a serious drawback since we

do not expect a two-parameter correlation to work in the critical

region.

3.2 Extension to Mixtures

We assume that the various pair direct correlation function

integrals in the mixture are given by a logical extension of Equation

(3-3). Thus we write,

$$C_{ij} = C_{ij}^{hs} - 2\rho(B_{ij} - B_{ij}^{hs}) \tag{3-14}$$

The i-j second virial coefficient is calculated by assuming the

standard mixing rules. We assume that the hard sphere mixture is one

with additive diameters and is described by the Carnahan-Starling

equation for mixtures (see Appendix B). Further, we assume that the

hard sphere size of each component is given by a logical extension of

Equations (3-6) and (3-7); that is, the reduced hard sphere size of

component i depends on the energy of interaction (T) relative to the

characteristic energy of the i-i interaction (T_i^*), and also on some

average reduced density which is the same for all components.

Thus we use the reduced second virial coefficient correlation

(Equations (3-4) and (3-5)) and the reduced hard sphere diameter

correlations (Equations (3-6) and (3-7)) as

$$B_{2_{ij}} = f_1(T/T^*_{ij}) \qquad (3-15)$$

$$\frac{\frac{2\pi}{3} N_{av}\sigma^3_{ii}}{V^*_{ii}} = f_2(T/T^*_{ii}, \rho V^*_m) \qquad (3-16)$$

where f_1 represents Equations (3-4) and (3-5) and f_2 represents Equations (3-6) and (3-7). The mixing rules employed are:

$$V^*_{ij} = \frac{1}{8}(V^{*1/3}_{ii} + V^{*1/3}_{jj})^3 \; ; \quad V^*_{ii} = V^*_i \qquad (3-17)$$

$$T^*_{ij} = (T^*_{ii} T^*_{jj})^{1/2} (1-K_{ij}) \; ; \quad T^*_{ii} = T^*_i \qquad (3-18)$$

$$V^*_m = \sum_{i,j} x_i x_j V^*_{ij} \qquad (3-19)$$

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \qquad (3-20)$$

where K_{ij} is a binary interaction parameter which must be evaluated from binary data.

This completes the description of the model for the pair direct correlation function integrals. We can only make qualitative arguments for its validity. Quantitative justification (or rejection) rests on comparison with experimental data.

Incidentally, we had previously used a different model for the pair direct correlation function integrals which was based on molecular theory. Although we do not use this model, we have given a brief description of it in Appendix A.

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CHAPTER 4
APPLICATION TO PURE FLUIDS--PARAMETER DETERMINATION

The model for the direct correlation function integrals can be used as an equation of state for pure fluids. If the characteristic parameters for a particular substance are known, then the change in pressure resulting from an isothermal change in density from ρ^r to ρ^f can be calculated according to

$$P^f - P^r = RT \int_{\rho^r}^{\rho^f} (1-C)d\rho \qquad (4-1)$$

Also, if the change in pressure is given, ρ^f can be calculated iteratively from Equation (4-1). We expect the use of our model in Equation (4-1) to be valid over a large range of conditions for simple substances (e.g., nitrogen or methane) but to be limited to the dense fluid region ($\rho/\rho_c > 1.5$ except at reduced temperatures greater than 2) for more complex substances which are nonrigid or have strong orientation dependent forces.[1,2] Clearly, Equation (4-1) can be used in a least-squares scheme to correlate compression data by fitting the two characteristic parameters, T^* and V^*. But, more importantly, such a scheme provides a means of estimating the characteristic parameters for use in predicting liquid mixture properties.

Table 4-1 shows the results of fitting the compression data of a wide range of substances; we have employed a nonlinear fitting

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Table 4-1

Fitting of Pure Component Compression Data

Name	T_c^a,K	V_c^a, cc/gmol	T^*,K	V^*, cc/gmol	Av. Abs. %[d] Error	Temp. range, K	Refs.
Argon (Krypton,Xenon)	150.8	75.4	150.7[b]	75.4[b]	0.61	90-423	3-9,23
Hydrogen	43.6[c]	51.5[c]	38.6	53.2	0.23	298-773	10
Nitrogen	126.2	89.5	126.3	90.9	1.98	77-234	11
Oxygen	154.6	73.4	154.0	74.1	2.24	90-327	11
Carbondioxide	304.2	94.0	291.1	91.8	4.25	245-473	11
Methane	190.6	99.0	192.0	99.8	1.31	112-376	11
Ethane	305.4	148.0	293.4	150.0	1.31	310-510	12
Propane	369.8	203.0	371.1	202.7	6.46	311-511	12
n-Butane	425.2	255.0	420.2	256.9	8.50	311-511	12
n-Pentane	469.6	304.0	508.4	320.3	7.09	311-511	12
n-Hexane	507.4	370.0	527.8	372.0	3.01	311-511	13
n-Octane	568.8	492.0	580.5	487.7	2.38	403-533	14
n-Nonane	594.6	548.0	677.9	553.6	2.04	303-423	15
n-Decane	617.6	603.0	678.8	616.1	1.40	298-358	16
n-Dodecane	658.3	713.0	686.9	739.8	1.03	298-358	16
n-Hexadecane	717.0	--	767.9	991.9	1.43	298-358	16
n-Heptadecane	733.0	1000.	845.2	1056.6	2.25	333-543	28
Benzene	562.1	259.0	571.9 / 575.1	256.9 / 258.8	2.08 / 0.41	403-543 / 298-353	14 / 21
Carbontetrachloride	556.4	276.0	586.3	280.7	0.47	298-358	29

Table 4-1 (Continued)

Name	T_c^a, K	V_c^a, $\frac{cc}{gmol}$	T^*, K	V^*, $\frac{cc}{gmol}$	Av. Abs. $\%^d$ Error	Temp. range, K	Refs.
Bromobenzene	670.0	324.0	577.6	325.6	0.51	298-358	22
Aniline	699.0	270.0	605.6	289.9	0.27	298-358	22
Nitrobenzene	725.0	340.0	608.2	327.0	0.26	298-358	22
Methanol	512.6	118.0	512.8	102.8	1.43	323-473	17
Ethanol	516.3	167.0	469.9	158.7	1.18	293-353	29
Water	647.3	56.0	295.8	46.5	0.78	298-358	29
			323.4	46.2	1.76	298-423	15
			438.7	46.4	1.64	273-373	18
Ethylene glycol	645	186.0	521.1	172.2	0.36	298-358	29
Ammonia	405.6	72.5	392.3	66.0	7.24	283-473	19
			360.2	65.1	2.21	253-313	20
4,4-Dipropylheptane	--	--	706.5	779.6	1.83	303-373	15
Tetraethylsilane	--	--	701.4	591.6	2.36	303-423	15
5,5-Dibutylnonane	--	--	767.6	1032.5	2.19	303-433	15
3,3-Diethylpentane	610.0	--	687.5	532.9	2.52	303-423	15
Tetraethylammonium tetrapropylborate	--	--	817.3	641.7	0.60	363-403	15
Tetrabutylammonium tetrabutylborate	--	--	942.4	1010.5	0.62	393-433	15
Tetrapropylammonium tetraethylborate	--	--	842.6	638.6	1.38	393-433	15

[a] All critical constants listed are from the Property Data Bank in Reference 24, except for hydrogen[25] and nitrobenzene;[26] [b] Values used in original fitting (Streett and Staveley[27]); [c] Pseudocritical constants;

[d] Av. Abs. % Error $= \frac{100}{n_d} \sum_{i=1}^{n_d} |(P_i^{cal} - P_i^{exp})|/P_i^{exp}$

subroutine to find the characteristic parameters which minimized the
sum of the squares of the differences between the calculated and
experimental pressure changes caused by isothermal density changes.
The average error in most cases is quite small and we see that the
model provides a fairly good description of liquid compressibilities.
The average errors for n-butane and n-pentane are quite high, but
this is so mostly because the data are close to the critical region.
Also, at high densities the isothermal compressibility predicted by
the model is too high and therefore in the fitting we have ignored
data points where the reduced density is greater than 3.65. However,
this normally corresponds to pressures well beyond those for chemical
processing. For example, at T = 318K and $\tilde{\rho}$ = 3.68 the pressure of
n-decane is 3743 atm. Yet, the correlation yields fairly good results
even in this case.

As we have stated above, the most important purpose of fitting
pure component data is to obtain accurate estimates of the charac-
teristic parameters. But while the method provides reliable estimates
of V^*, T^* can be varied within a fairly large range. (This is to be
expected since Brelvi and O'Connell[2] have shown that, to a high degree
of accuracy, liquid compressibility data can be correlated by a size
parameter only.) Figure 4-1 shows a plot of the characteristic
parameters of the n-alkanes versus carbon number. The dashed lines
are the analogous curve for critical constants. The characteristic
volumes all fall on a smooth curve with no noticeable fluctuation.
They are slightly, but significantly, greater than the (estimated)
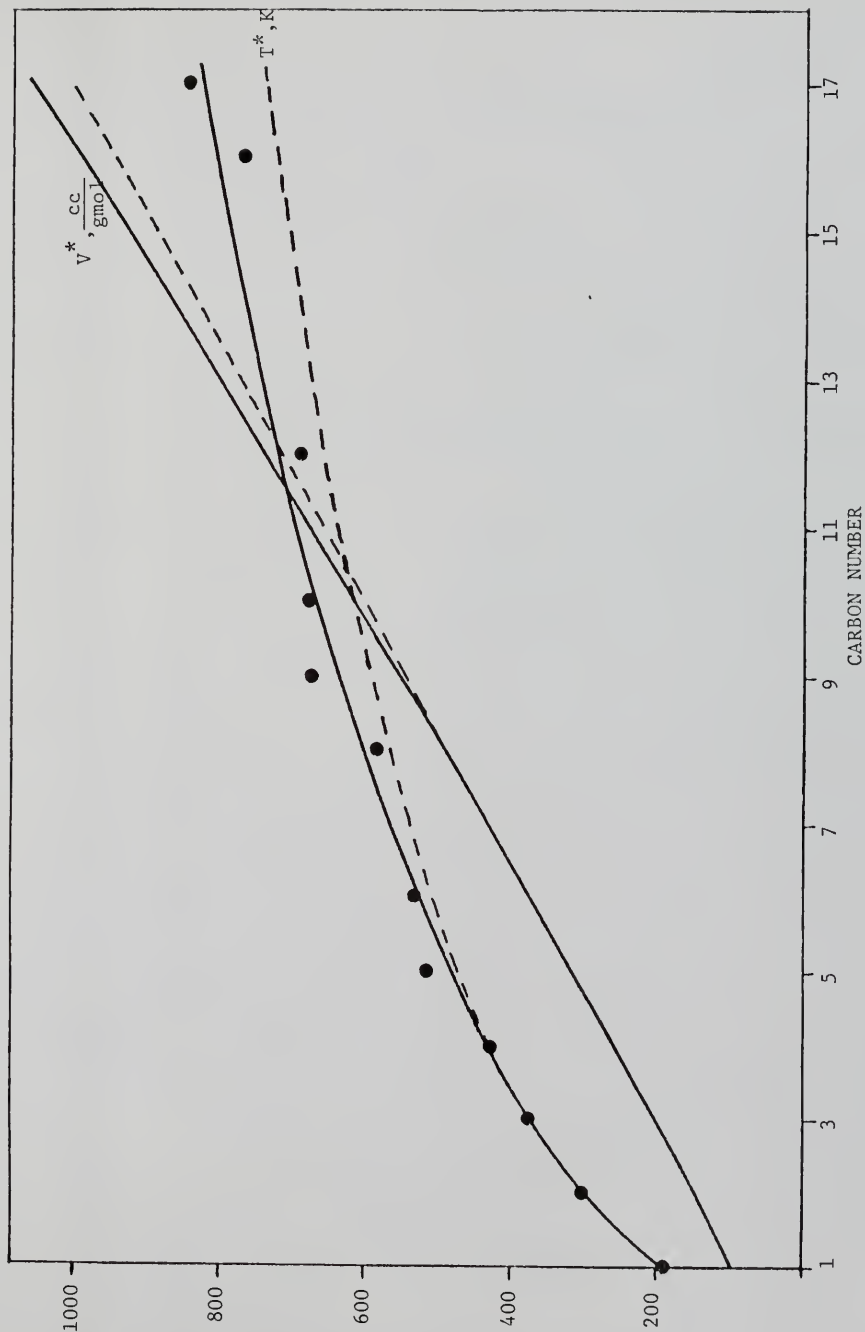
Figure 4-1. Smoothed variation of the characteristic parameters of the n-alkanes with carbon number. The dashed lines show the corresponding variation of the critical constants. The points show the individually fitted T* values

Table 4-2

Smoothed Values of Characteristic Parameters for
the Normal Paraffins

	Fitted Parameters		Smoothed Parameters	
	T^*	V^*	T^*	V^*
Methane	192.0	99.8	192.0	99.8
Ethane	293.4	150.0	293.4	150.0
Propane	371.1	202.7	371.1	202.7
n–Butane	420.2	256.9	425.0	257.3
n–Pentane	508.4	320.3	480.0	318.8
n–Hexane	527.8	372.0	527.8	372.0
n–Octane	580.5	487.7	600.0	487.7
n–Nonane	677.9	553.6	640.	554.8
n–Decane	678.8	616.1	670.	616.1
n–Dodecane	686.9	739.8	720.	738.7
n–Hexadecane	767.9	991.9	810.	992.0
n–Heptadecane	845.2	1056.6	830.	1057.

critical volumes for the higher members of the homologous series. The variation of the fitted characteristic temperature shows large fluctuations (indicated by the points in Figure 4-1), so we have drawn a rough average curve through the points. Again, as for the size parameter, T^* is greater than the (estimated) T_c for the larger n-alkanes. Table 4-2 shows the smoothed parameters for this series.

The predicted behavior of binary systems is generally not sensitive to T^* and hence an accurate estimation of this parameter is not crucial for this purpose. But for multicomponent systems we also have to insure that Henry's constants of a solute in many solvents are mutually consistent. In this case, if the values of T^* are not appropriate, the values of the binary interaction para- meters from Henry's constants will be different from those for the correct deviation from Henry's Law. Thus, for multicomponent systems a reasonably accurate estimate of T^* is necessary.

One way of obtaining consistent values of the parameters is to adopt the method we have used for the n-alkanes. Another method-- one which we have employed to a limited extent (see Chapter 6)--is to evaluate the parameters to insure consistency between pure component and mixture data. In any event, if only pure component data are used, they should cover a wide range of temperatures; pure component data over a single isotherm will not be sufficient to obtain the charac- teristic temperature.

For the n-alkanes T^* and V^* are greater than or equal to the corresponding critical constants. This appears to be a general trend

for all nonpolar molecules. For strongly polar molecules, V^* is significantly smaller than V_c and T^* is, in general, less than T_c. These are however only qualitative trends and there do not appear to be any quantitative relations for our parameters in terms of any other parameters. Because of the sensitivity of the results to the value of V^*, we are convinced that prediction of this quantity will be useless and only compression data will be adequate to obtain appropriate values.

<h2 style="text-align:center">References for Chapter 4</h2>

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CHAPTER 5
THERMODYNAMIC PROPERTIES OF BINARY GAS-SOLVENT
SYSTEMS; CORRELATION

Gas-solvent binaries provide a straightforward application of
the method we have developed. By a gas-solvent system we mean any
system which contains a supercritical component (the gas or solute)
and a subcritical component (the solvent). For this type of system
the most convenient (unique) reference state is the pure, saturated
solvent at the temperature of the system. Let subscript 1 refer to
the solute and subscript 2 to the solvent. Now Equation (1-2) can be
written as

$$\ln f_1^L(P,T,x_1) = \ln H_{12}(P^r,T,x_1=0) + \ln x_1 + \ln \gamma_1(P,T,x_1) \quad (5-1)$$

$$\ln f_2^L(P,T,x_1) = \ln f_2^r(P^r,T,x_1=0) + \ln x_2 + \ln \gamma_2(P,T,x_1) \quad (5-2)$$

where H_{12} is Henry's constant of the gas in the pure, saturated solvent
and f_2^r is the fugacity of the solvent at the reference state. Our
method can be used to predict the activity coefficients so if the refer-
ence fugacities are available we can calculate the liquid-phase fugac-
ities. These can then be used together with some vapor-phase equation
of state to predict vapor-liquid equilibria.

In this chapter we describe our correlation of gas-solvent
vapor-liquid equilibrium by using our method to calculate liquid-

phase nonidealities. Before describing our work, we give a review
of other work on the same problem and also show some experimental
results to demonstrate that it is advantageous to adopt our approach.

5.1 Review of Existing Work

The first attempt to correlate the nonideality of gas-solvent
systems was that of Krichevskii.[1] He reasoned that since in these
systems the solubility of the solute is normally small, the com-
position nonideality can be neglected and deviations of the solute
fugacity from Henry's law are entirely due to the pressure. Therefore,
we can write,[2]

$$\ln f_1^L = \ln (H_{12}x_1) + \frac{1}{RT} \int_{P_2^S}^{P} \overline{V}_1^{\infty} \, dP \qquad (5-3)$$

Further, if we assume that the infinite dilution partial molar
volume of the solute is independent of pressure (a reasonable assump-
tion if the temperature is not close to the critical temperature of
the solvent), Equation (5-3) simplifies to

$$\ln f_1^L = \ln (H_{12}x_1) + \frac{\overline{V}_1^{\infty}}{RT} (P - P_2^S) \qquad (5-4)$$

Equation (5-4) indicates that $\ln (f_1^L/x_1)$ varies linearly with
pressure which is so for many gas-solvent binaries. However, Equation
(5-4) also indicates that the slope of the linear variation is equal
to $\overline{V}_1^{\infty}/RT$ which is not generally observed. The partial molar volume
obtained from this slope is invariably different from the experimental

partial molar volume of the solute. The apparent anomaly has been explained by Orentlicher and Prausnitz,[3] and by Gibbs and Van Ness[4] who showed that the composition nonideality must also be accounted for. These authors employ the simple but thermodynamically consistent expression,[2]

$$RT \ln \gamma_1^{x^*} = A(x_2^2 - 1) \tag{5-5}$$

where A (the two-suffix Margules equation constant) depends on temperature, but not on pressure or composition. Following Prausnitz[2] we use the superscript * to indicate that γ_1^x is normalized in the unsymmetric convention.

The reason why γ_1^x is significant even at small values of x_2 is that its first derivative at the reference state is nonzero

$$\lim_{x_1 \to 0} \frac{\partial \ln \gamma_1^*}{\partial x_1} = -\frac{2A}{RT} \tag{5-6}$$

An expression for γ_2^x can be obtained from that for $\gamma_1^{x^*}$ by using the Gibbs-Duhem equation[2]

$$RT \ln \gamma_2^x = A x_1^2 \tag{5-7}$$

The quantity necessarily has a zero composition derivative at the reference state.

$$\lim_{x_1 \to 0} \frac{\partial \ln \gamma_2}{\partial x_1} = 0 \tag{5-8}$$

Therefore, it is reasonable to expect that an equation of the form (5-1) would be valid for the solvent component. However, for the solute, the composition nonideality must be accounted for. Using Equation (5-5) we obtain the Krichevskii-Ilinskaya equation,

$$\ln f_1^l = \ln (H_{12}x_1) + \frac{A}{RT} (x_2^2 - 1) + \frac{\overline{V}_1^\infty}{RT} (P - P_2^s) \quad (5-9)$$

At small values of x_1 Equation (5-9) reduces to[3]

$$\ln f_1^l = \ln (H_{12}x_1) + \left| \overline{V}_1^\infty - \frac{2A}{H_{12}\phi_1^s - P_2^s} \right| \frac{P - P_2^s}{RT} \quad (5-10)$$

where ϕ_1^s is the fugacity coefficient of the solute at infinite dilution in the saturated solvent. Therefore, even if the composition non-ideality is taken into account, $\ln (f_1^L/x_1)$ varies linearly with pressure, but the slope is different from that given by Equation (5-4).

Orentlicher and Prausnitz[3] have used Equation (5-10) to cor-relate the solubility of hydrogen in cryogenic solvents at high pressures. Their correlation of the quantities $\overline{V}_1^\infty$ and A was essentially deduced from the experimental data. Therefore, it is specific to the solute hydrogen. Further, their approach is to correlate the two quantities separately. But, as their results show, the composition nonideality provides a significant cancellation of the pressure nonideality. For example, for the system hydrogen-carbon monoxide at 88K:

$$\overline{V}_1^\infty = 34.4 \quad \text{cc/g mole}$$

$$\frac{2A}{H_{12}\phi_1^s - P_2^s} = 35. \quad \text{cc/g mole}$$

and for the system hydrogen-propane at 282K:

$$\overline{V}_1^\infty = 63 \quad \text{cc/g mole}$$

$$\frac{2A}{H_{12}\phi_1^s - P_2^s} = 48.5 \quad \text{cc/g mole}$$

(The above results were obtained from Table 2 of Reference 3.)

Therefore, as we have mentioned in Chapter 1, from the engi-
neering point of view, it is advantageous to have a single model
which accounts for both these corrections.

A further disadvantage of a representation of the form of
Equation (5-7) is that at high temperatures $(T/T_c^{solvent} \gtrsim 0.88)$ the
assumption that the partial molar volume is independent of pressure
is not valid. Thus, under these conditions, the variation of the
partial molar volume with pressure--and with composition--must be
taken into account. If such a description is thermodynamically
consistent, it must be consistent with the description of the com-
position nonideality. Surprisingly, our experience is that the
total deviations from ideality remain relatively small even when
all of these variations occur.

5.2   Some Features of Gas-Solvent Nonideality--The Carbon monoxide-Benzene System

The features of fugacity variation of gas-solvent systems we have been trying to describe are elucidated by the experimental data on the Carbon monoxide-Benzene system.[6]   Figure 5-1 shows the variation of $\ln (f_{co}/x_{co})$ with pressure.   The full line represents the experimental quantity; the dashed line shows the prediction of the fugacity if the pressure correction alone is assumed, and the horizontal line gives the fugacity if Henry's law were obeyed.   The main feature to be observed is that the total nonideality correction is very much less in magnitude than either the pressure correction or the composition correction alone.   The 533.15K isotherm is a good illustration of the opposing effects of the two nonideality corrections.   At lower pressures, the Poynting correction is slightly greater than the composition effect so the product is greater than unity.   As the pressure increases, the composition correction increases relatively faster   and the product becomes less than unity. Yet, over the whole pressure range the total correction to Henry's law remains quite small.

Figure 5-2 is the analogous plot for the solvent component, benzene.   In this case, the correction is simply due to pressure since the composition does not change materially.   Our theory (Equation (5-8)) describes the effect very well.   Recall that the solvent saturated density is input data and our parameters are obtained by fitting compressibility data.   Whatever small changes there are in density due to pressure will be correlated very well
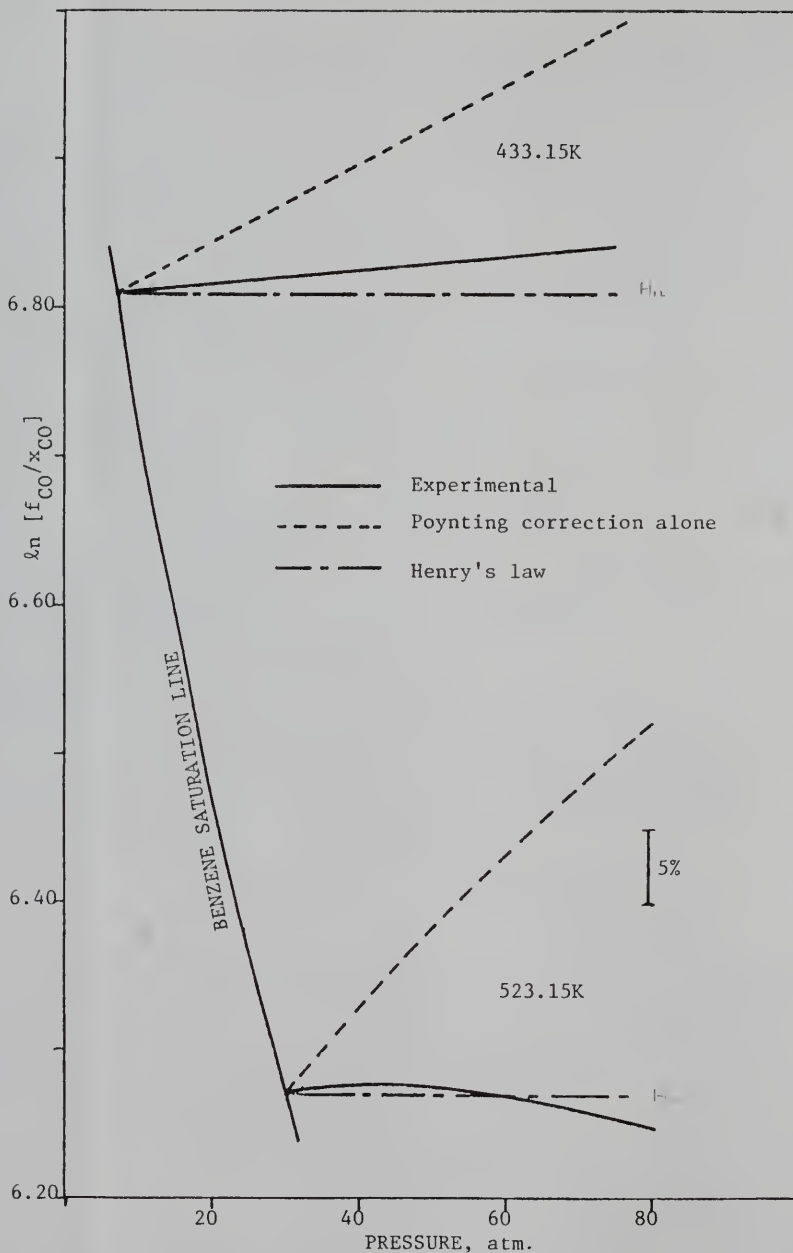
Figure 5-1. Experimental variation of the nonideality of carbon monoxide in carbon monoxide-benzene solutions (Connolly[6])
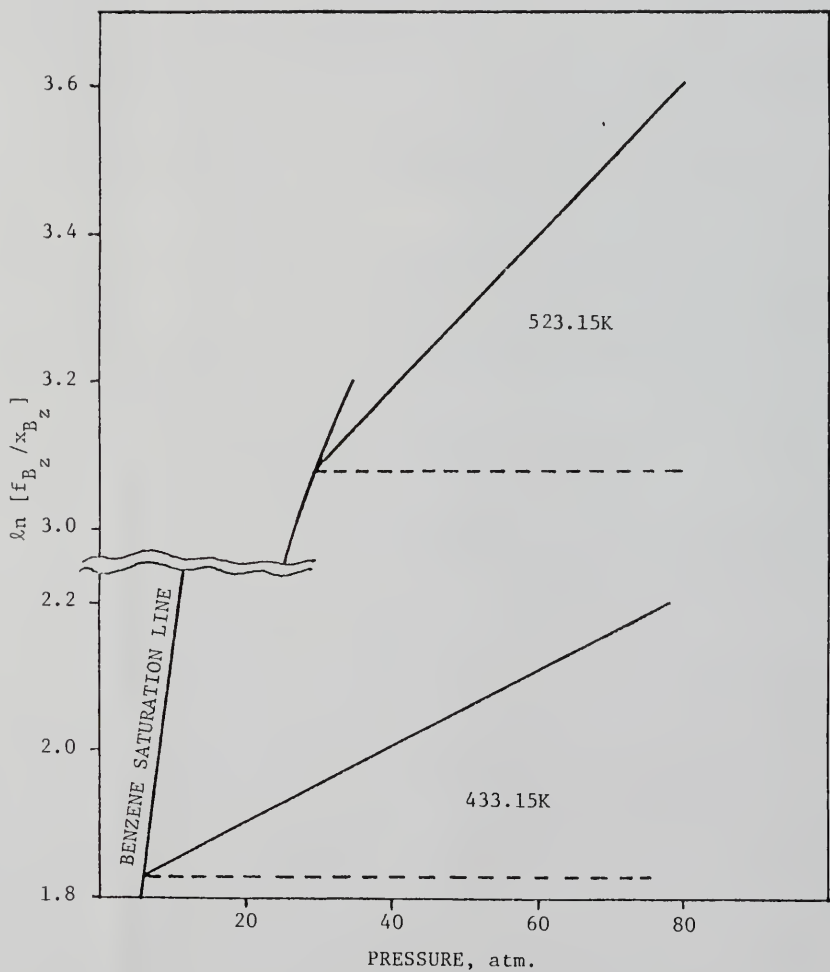
Figure 5-2. Experimental variation of the nonideality of
benzene in carbon monoxide–benzene solutions
(Connolly[6]). The Poynting correction factor
and activity coefficient coincide within
experimental error

and we can always expect a very accurate estimate of the solvent
activity coefficient if the solute concentration is small.

5.3 Correlation of Experimental Data

One way to test the validity of our method is to calculate
the nonideality from experimental data and then compare it with the
prediction of the model. But this could lead to invalid conclusions
since it is difficult to gauge the effect of an error in the activity
coefficients on the predicted equilibrium. Besides, the aim of our
model is to obtain predictions of phase equilibrium. Thus we test
our model by using it as part of a scheme to predict vapor-liquid
equilibrium. We do so at the risk that when errors appear, we cannot
be sure where to attribute them.

The use of our method to obtain liquid-phase fugacities
requires information about the reference state: the saturation
density and pressure of the solvent and Henry's constant of the gas
in the solvent.

The description of the vapor phase must be obtained from a
valid equation of state. The modified Redlich-Kwong equation[7] provides
an adequate description of nonpolar and slightly polar mixtures. Several
excellent 2nd virial coefficient correlations[8,9] are available, but the
virial expansion truncated at the second term is valid only at low
densities. An equation called the perturbed-hard-sphere equation[10]
has been proposed for gas mixtures containing polar components. This
equation appears to provide a reasonably accurate description of gas
mixtures containing components whose parameters are listed in the

original paper, but there is no way to obtain accurate estimates of
the parameters for new substances. We have used the most appropriate
of the above three vapor-phase equations depending on the binary
system involved.

The method we have used to correlate gas-solvent data is very
similar to the one proposed by Barker.[11] We employ a simple empirical
form for Henry's constant:

$$\ln H_{12} = a_0 + a_1 T + a_2 T^2 \tag{5-11}$$

where a_0, a_1, a_2 are constants to be determined from P-T-X data. Values
of x_1 and y_1 were calculated from each P and T data point using the
various equations for vapor and liquid fugacities, then a nonlinear
fitting subroutine was used to find the value of the constants
$a_0 - a_2$ which minimized the sum of squares between the calculated
and experimental liquid mole fractions, X_1. When available, the
experimental vapor mole fractions were compared with the calculated
value. This provides a further consistency check on the data and
the correlations.

All the pure component parameters (T^* and V^*) used have been
obtained from pure component compressibility data (see Tables 4-1
and 4-2) except for carbon monoxide where we assumed the parameters are
equal to the corresponding critical constants. The binary interaction
parameters must be estimated from the binary data. Fortunately, in
many cases the predicted activity coefficients are insensitive to its
value. For these systems we have set $K_{12} = 0$, thus actually predicting

the liquid nonideality from pure component data alone. In cases
where a nonzero value of K_{12} is required, we have estimated its
value by fitting the data with various values of the parameters and
picking the one we thought gave the best overall fit.

Tables 5-1 - 5-17 show a comparison of the calculated and
experimental liquid and vapor composition for a wide variety of
gas-solvent binary systems; we also show the predicted activity
coefficients. Rows in these tables which are denoted by a * cor-
respond to data points which were not considered in the fitting; we
consider these points to be beyond the range of applicability of the
theory, i.e., too close to the critical. This is usually detected
by the experimental value of y_1 decreasing with increasing pressure,
X_1 greater than 0.4 or $T/T_c > 0.9$. Table 5-18 summarizes the results
of the correlation.

The theory provides excellent predictions of the liquid-phase
nonidealities of all the systems considered except for the carbon
monoxide-methanol system. Figure 5-3 shows the calculation of the
liquid mole fractions for the system carbon monoxide-benzene. We see
that the results are very close to the experimental data. From
Table 5-1 we see that the predicted vapor compositions are quite
close to the experimental values, but the mole fraction of the gas
is slightly high. This is a feature common to most systems we have
investigated, but we cannot account for the precise reason why this
is so. We have used a nonzero value of the binary interaction
parameter for this binary. Its value is equal to the value obtained
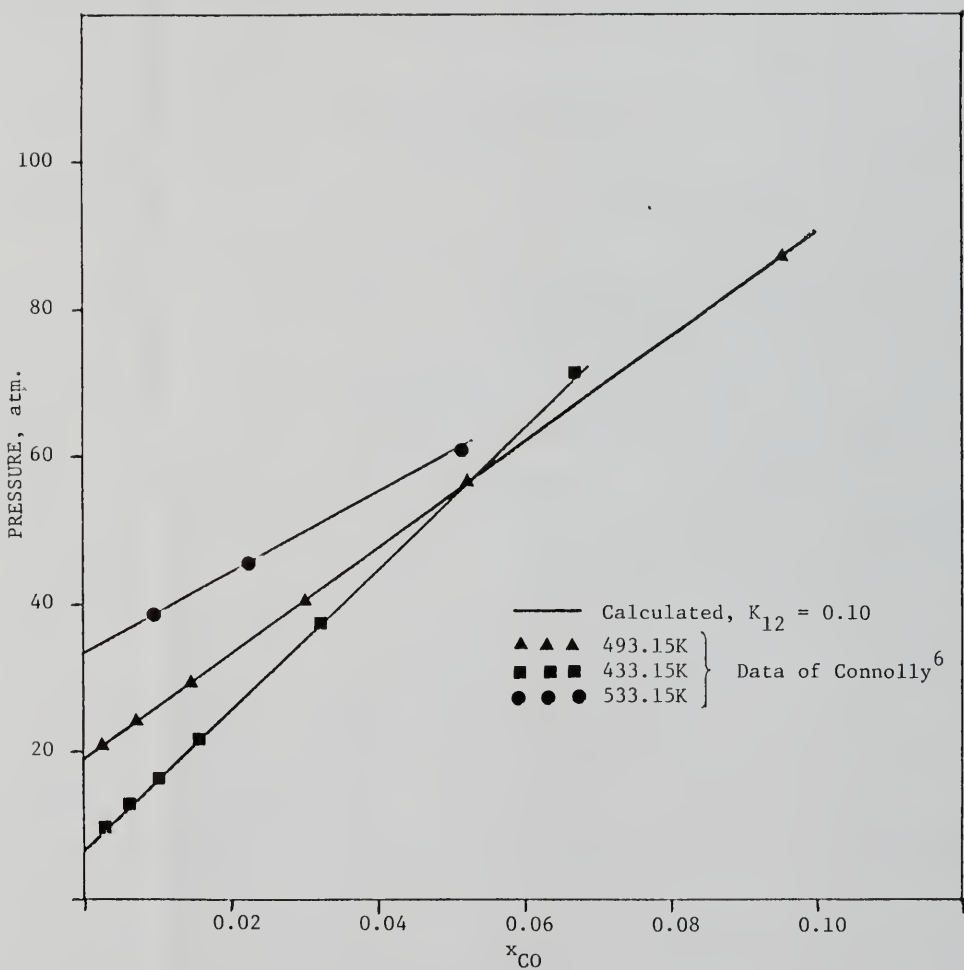
Figure 5-3. Solubility of carbon monoxide in benzene

Table 5-1

Carbon monoxide (1)-Benzene (2), $K_{12} = 0.10$

T,K	P, atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
433.2	9.9	.00309	.00320	.2585	.2511	1.00	1.01
	12.8	.00615	.00637	.4037	.4089	1.00	1.02
	16.4	.00993	.01026	.5202	.5226	1.01	1.03
	21.7	.01553	.01603	.6186	.6242	1.01	1.05
	37.6	.03228	.03313	.7562	.7592	1.02	1.10
	71.1	.06714	.06797	.8377	.8441	1.04	1.22
443.2	12.1	.00402	.00413	.2585	.2624	1.00	1.01
	15.7	.00796	.00818	.4037	.4084	1.00	1.02
	20.3	.01301	.01334	.5202	.5239	1.01	1.04
	27.0	.02042	.02088	.6186	.6245	1.01	1.06
	48.7	.04404	.04465	.7562	.7601	1.03	1.13
	103.2	.10340	.10220	.8377	.8472	1.07	1.34
453.2	12.3	.00253	.00259	.1475	.1499	1.00	1.01
	14.6	.00518	.00529	.2585	.2624	1.00	1.01
	19.1	.01032	.01053	.4037	.4088	1.01	1.03
	25.0	.01700	.01732	.5202	.5249	1.01	1.05
	33.6	.02688	.02730	.6186	.6249	1.02	1.07
	63.5	.06099	.06112	.7562	.7615	1.03	1.18
463.2	14.7	.00324	.00331	.1475	.1499	1.00	1.01
	17.6	.00665	.00679	.2585	.2627	1.00	1.02
	23.2	.01338	.01363	.4037	.4102	1.01	1.03
	30.6	.02226	.02261	.5202	.5263	1.01	1.06
	41.8	.03563	.03601	.6186	.6257	1.02	1.10
	85.8	.08837	.08732	.7562	.7649	1.05	1.26
473.2	17.5	.00418	.00426	.1475	.1508	1.00	1.01
	21.1	.00860	.00877	.2585	.2638	1.00	1.02
	28.1	.01741	.01770	.4037	.4113	1.01	1.04
	37.3	.02900	.02937	.5202	.5251	1.01	1.07
	52.4	.04792	.04819	.6186	.6269	1.02	1.13
483.2	20.7	.00537	.00549	.1475	.1513	1.00	1.01
	25.0	.01106	.01129	.2585	.2636	1.00	1.03
	33.9	.02270	.02309	.4037	.4118	1.01	1.05
	45.8	.03839	.03883	.5202	.5254	1.01	1.09
	66.5	.06588	.06593	.6186	.6269	1.02	1.17
493.2	21.5	.00298	.00304	.0698	.0722	1.00	1.01
	24.3	.00693	.00707	.1475	.1510	1.00	1.02
	29.7	.01440	.01468	.2585	.2637	1.00	1.03

Table 5-1 (Continued)

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
	40.9	.02993	.03040	.4037	.4117	1.01	1.07
	56.9	.05239	.05283	.5202	.5272	1.01	1.13
	87.3	.09591	.09514	.6186	.6302	1.02	1.24
503.2	25.0	.00381	.00388	.0698	.0711	1.00	1.01
	28.5	.00900	.00916	.1475	.1504	1.00	1.02
	35.2	.01890	.01924	.2585	.2638	1.00	1.04
	49.6	.04014	.04071	.4037	.4110	1.01	1.09
	72.3	.07434	.07471	.5202	.5275	1.01	1.17
513.2	28.9	.00501	.00507	.0698	.0710	1.00	1.01
	33.3	.01185	.01203	.1475	.1498	1.00	1.02
	41.8	.02524	.02562	.2585	.2630	1.00	1.05
	61.0	.05592	.05651	.4037	.4097	1.00	1.12
	98.1	.11897	.11889	.5202	.5330	0.98	1.28
523.2	33.5	.00672	.00673	.0698	.07C8	1.00	1.01
	38.9	.01594	.01601	.1475	.1483	1.00	1.03
	50.0	.03487	.03510	.2585	.2596	0.99	1.07
	78.1	.08504	.08529	.4037	.4079	0.97	1.18
533.2	38.6	.00913	.00886	.0980	.0683	1.00	1.02
	45.8	.02252	.02207	.1475	.1459	0.99	1.04
	61.0	.05145	.05083	.2585	.2536	0.97	1.10

RMS deviation in x_1 = 0.0004

Table 5-2

Carbon monoxide (1)-n-Octane (2), K_{12} = 0.21

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
463.2	6.6	.00488	.00464	.2750	.2655	1.00	1.01
	8.3	.00891	.00890	.4059	.4130	1.01	1.02
	10.4	.01366	.01364	.5092	.5161	1.01	1.03
	14.4	.02287	.02280	.6277	.6361	1.02	1.06
	23.3	.04285	.04259	.7499	.7577	1.03	1.11
473.2	8.1	.00635	.00636	.2750	.2805	1.00	1.01
	10.3	.01160	.01161	.4059	.4131	1.01	1.03
	12.9	.01787	.01788	.5092	.5167	1.01	1.04
	18.1	.03011	.03008	.6277	.6369	1.02	1.07
	29.7	.05707	.05678	.7499	.7582	1.04	1.14
483.2	9.8	.00823	.00827	.2750	.2803	1.01	1.02
	12.6	.01509	.01515	.4059	.4130	1.01	1.03
	16.0	.02336	.02344	.5092	.5170	1.01	1.05
	22.7	.03976	.03981	.9277	.6378	1.03	1.09
	38.6	.07806	.07768	.7499	.7620	1.05	1.20
493.2	9.7	.00500	.00504	.1528	.1552	1.00	1.01
	11.9	.01073	.01080	.2750	.2804	1.01	1.02
	15.4	.01976	.01988	.4059	.4134	1.01	1.04
	19.7	.03076	.03094	.5092	.5187	1.02	1.07
	28.5	.05297	.05314	.6277	.6400	1.03	1.12
	51.1	.10912	.10850	.7499	.7666	1.06	1.28
503.2	10.2	.00274	.00276	.0702	.0721	1.00	1.01
	11.6	.00654	.00660	.1528	.1556	1.00	1.01
	14.4	.01405	.01418	.2750	.2805	1.01	1.03
	18.8	.02598	.02622	.4059	.4143	1.01	1.06
	24.4	.04080	.04114	.5092	.5194	1.02	1.09
	36.1	.07187	.07223	.6277	.6411	1.04	1.17
513.2	12.1	.00360	.00362	.0702	.0718	1.00	1.01
	13.9	.00862	.00868	.1528	.1551	1.00	1.02
	17.3	.01860	.01873	.2750	.2798	1.01	1.04
	23.0	.03473	.03500	.4059	.4144	1.02	1.07
	30.3	.05518	.05560	.5092	.5198	1.02	1.12
533.2	16.7	.00651	.00637	.0702	.0697	1.00	1.01
	19.6	.01578	.01554	.1528	.1519	1.00	1.03
	25.3	.03453	.03428	.2750	.2748	1.01	1.07
	35.5	.06717	.06729	.4059	.4077	1.01	1.13

RMS deviation in x_1 = 0.0002

Table 5-3

Hydrogen (1)-Benzene (2), K_{12} = 0.0

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
433.2	20.7	.00890	.00925	.6147	.6186	1.02	1.04
	32.0	.01615	.01673	.7376	.7418	1.03	1.08
	51.4	.02846	.02931	.8285	.8295	1.06	1.15
	89.0	.05145	.05242	.8897	.8904	1.10	1.28
	113.0	.06601	.06644	.9081	.9085	1.14	1.38
443.2	18.8	.00715	.00739	.4921	.4990	1.01	1.03
	25.5	.01182	.01219	.6147	.6189	1.02	1.05
	39.8	.02149	.02207	.7376	.7415	1.04	1.10
	64.9	.03822	.03893	.8285	.8292	1.07	1.19
	115.6	.07053	.07071	.8897	.8904	1.14	1.38
	150.2	.09159	.09087	.9081	.9089	1.19	1.53
453.2	22.8	.00938	.00967	.4921	.4982	1.02	1.04
	31.4	.01562	.01605	.6147	.6191	1.03	1.07
	49.3	.02853	.02913	.7376	.7413	1.05	1.13
	82.1	.05139	.05187	.8285	.8285	1.10	1.24
	151.7	.09734	.09600	.8897	.8909	1.20	1.53
463.2	22.2	.00801	.00826	.3902	.3946	1.01	1.03
	27.7	.01233	.01269	.4921	.4980	1.02	1.05
	38.4	.02061	.02113	.6147	.6189	1.04	1.08
	61.1	.03787	.03850	.7376	.7410	1.07	1.16
	104.2	.06937	.06948	.8285	.8287	1.13	1.32
473.2	33.5	.01621	.01672	.4921	.4982	1.03	1.06
	46.8	.02718	.02787	.6147	.6187	1.04	1.10
	75.8	.05042	.05112	.7376	.7408	1.09	1.21
	134.0	.09478	.09401	.8285	.8299	1.17	1.43
483.2	32.0	.01387	.01439	.3902	.3956	1.02	1.05
	40.4	.02136	.02208	.4921	.4979	1.03	1.08
	57.2	.03605	.03701	.6147	.6188	1.06	1.13
	94.5	.06764	.06836	.7376	.7408	1.11	1.27
	175.7	.13175	.12894	.8285	.8326	1.24	1.61
493.2	38.2	.01825	.01902	.3902	.3947	1.03	1.06
	48.7	.02824	.02928	.4921	.4970	1.04	1.09
	70.0	.04811	.04937	.6147	.6177	1.07	1.17
	119.2	.09212	.09243	.7376	.7405	1.15	1.36
503.2	45.6	.02425	.02535	.3902	.3934	1.03	1.08
	58.9	.03779	.03924	.4921	.4974	1.05	1.12

Table 5-3 (Continued)

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
	86.4	.06510	.06668	.6147	.6169	1.09	1.22
	153.9	.12863	.12766	.7376	.7438	1.20	1.50
513.2	36.7	.01253	.01323	.2027	.2044	1.02	1.04
	54.8	.03282	.03431	.3902	.3939	1.04	1.10
	71.7	.05147	.05333	.4921	.4963	1.07	1.16
	108.1	.09030	.09185	.6147	.6178	1.12	1.30
523.2	35.4	.00741	.00779	.0998	.1003	1.01	1.02
	43.2	.01725	.01809	.2027	.2037	1.02	1.05
	85.5	.06839	.07038	.4921	.4826	1.08	1.20
	140.1	.13163	.13079	.6147	.6247	1.17	1.42
533.2	41.0	.01041	.01078	.0998	.0986	1.01	1.03
	81.6	.06602	.06661	.3902	.3830	1.07	1.17
	113.2	.10802	.10642	.4921	.4994	1.13	1.30

RMS deviation in x_1 = 0.0010

Table 5-4

Hydrogen (1)-n-Octane (2), $K_{12} = 0.0$

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
463.2	9.9	.00869	.00913	.4954	.5015	1.01	1.03
	16.2	.01850	.01937	.6713	.6807	1.03	1.07
	27.2	.03554	.03697	.7959	.8026	1.05	1.13
	43.1	.05933	.06116	.8629	.8706	1.09	1.24
	62.8	.08741	.08916	.9004	.9074	1.13	1.37
473.2	12.3	.01152	.01204	.4954	.5019	1.02	1.04
	20.1	.02454	.02554	.9713	.6813	1.03	1.08
	34.4	.04755	.04905	.7959	.8045	1.07	1.17
	55.2	.07952	.08103	.8629	.8718	1.12	1.31
	82.0	.11837	.11882	.9004	.9100	1.19	1.51
483.2	15.1	.01525	.01595	.4954	.5027	1.02	1.05
	25.1	.03263	.03389	.6713	.6829	1.05	1.11
	43.6	.06361	.06527	.7959	.8069	1.09	1.23
	71.4	.10762	.10851	.8629	.8758	1.16	1.42
	108.6	.16150	.15938	.9004	.9140	1.26	1.73
493.2	10.6	.00538	.00568	.2107	.2129	1.01	1.02
	12.6	.00914	.00963	.3117	.3148	1.01	1.03
	18.5	.02024	.02125	.4954	.5037	1.03	1.06
	31.0	.04317	.04487	.6713	.6832	1.06	1.14
	55.0	.08493	.08679	.7959	.8094	1.12	1.30
	92.9	.14584	.14537	.8629	.8804	1.23	1.59
	148.5	.22479	.21691	.9004	.9209	1.38	2.11
503.2	12.8	.00716	.00762	.2107	.2132	1.01	1.02
	15.3	.01228	.01303	.3117	.3171	1.02	1.03
	22.6	.02693	.02842	.4954	.5039	1.04	1.08
	39.0	.05848	.06090	.6713	.6876	1.08	1.18
	70.1	.11466	.11662	.7959	.8130	1.17	1.40
	123.7	.20080	.19702	.8629	.8885	1.32	1.86
513.2	14.1	.00701	.00755	.1635	.1654	1.01	1.02
	15.2	.00956	.01027	.2107	.2127	1.01	1.03
	18.4	.01643	.01761	.3117	.3168	1.02	1.04
	27.7	.03617	.03843	.4954	.5059	1.05	1.10
	48.3	.07814	.08153	.6713	.6889	1.11	1.24
	91.2	.15784	.15923	.7959	.8231	1.23	1.56
523.2	18.2	.01304	.01415	.2107	.2127	1.02	1.03
	22.2	.02233	.02413	.3117	.3172	1.03	1.06
	34.1	.04926	.05262	.4954	.5064	1.06	1.13

Table 5-4 (Continued)

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
	61.7	.10862	.11315	.6713	.6999	1.14	1.32
	123.9	.22578	.22385	.7959	.8413	1.34	1.85
533.2	17.9	.00821	.00897	.1080	.1078	1.01	1.02
	19.9	.01323	.01444	.1635	.1630	1.02	1.03
	21.8	.01815	.01977	.2107	.2117	1.02	1.04
	26.9	.03112	.03372	.3117	.3152	1.04	1.08
	42.5	.06920	.07388	.4954	.5115	1.08	1.18
	80.4	.15525	.16005	.6713	.7169	1.20	1.46
543.2	21.2	.01193	.01298	.1080	.1054	1.01	1.03
	26.2	.02616	.02833	.2107	.2082	1.03	1.06
	33.0	.04454	.04844	.3117	.3137	1.05	1.10
	54.3	.10204	.10748	.4954	.5252	1.11	1.26
	115.8	.25001	.24641	.6713	.7658	1.32	1.80

RMS deviation in x_1 = 0.0025

Table 5-5

Hydrogen (1)-n-Hexane (2), K_{12} = 0.0

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2	
277.6	34.1	.02800	.02980	.9960	.9973	1.05	1.21	
	68.1	.05400	.05779	.9980	.9983	1.10	1.47	
	136.2	.09900	.10914	.9980	.9988	1.21	2.15	
	204.2	.14000	.15504	.9980	.9990	1.33	3.13	
	272.3	.17900	.19642	.9980	.9990	1.45	4.56	
	408.4	.25600	.26805	.9980	.9990	1.73	9.57	
	544.6	.33400	.32821	.9980	.9991	2.04	19.95	
	680.7	.42200	.37976	.9980	.9991	2.40	41.25	*
310.9	68.1	.05900	.06068	.9920	.9932	1.11	1.42	
	136.2	.10800	.11411	.9950	.9956	1.22	2.03	
	204.2	.15300	.16124	.9950	.9963	1.34	2.87	
	272.3	.19600	.20314	.9950	.9967	1.47	4.05	
	408.4	.27900	.27417	.9950	.9970	1.76	8.01	
	544.6	.36600	.33216	.9950	.9972	2.08	15.66	
	680.7	.46100	.38083	.9950	.9974	2.45	30.42	*
344.3	34.1	.03400	.03371	.9610	.9628	1.05	1.18	
	68.1	.06400	.06591	.9780	.9791	1.11	1.39	
	136.2	.11900	.12377	.9860	.9871	1.23	1.94	
	204.2	.16900	.17406	.9880	.9897	1.36	2.69	
	272.3	.21600	.21814	.9880	.9910	1.49	3.72	
	408.4	.30900	.29138	.9880	.9923	1.79	7.03	
	544.6	.40500	.34976	.9880	.9931	2.13	13.13	*
377.6	34.1	.03600	.03681	.9040	.9052	1.05	1.16	
	68.1	.07000	.07353	.9460	.9476	1.12	1.37	
	136.2	.13200	.13861	.9660	.9688	1.24	1.88	
	204.2	.18700	.19419	.9710	.9759	1.38	2.57	
	272.3	.24100	.24208	.9740	.9795	1.53	3.50	
	408.4	.34500	.31987	.9740	.9833	1.85	6.38	
	544.6	.45000	.38037	.9740	.9855	2.21	11.50	*
410.9	34.1	.03800	.03981	.7970	.7913	1.05	1.14	
	68.1	.07800	.08353	.8860	.8849	1.12	1.34	
	136.2	.14900	.15975	.9270	.9334	1.26	1.83	
	204.2	.21300	.22347	.9390	.9496	1.41	2.48	
	272.3	.27400	.27727	.9440	.9580	1.57	3.34	
	408.4	.39300	.36228	.9460	.9675	1.92	5.95	*
	544.6	.51100	.42653	.9440	.9725	2.31	10.47	*
444.3	34.1	.03700	.04097	.6060	.5938	1.05	1.12	
	68.1	.08600	.09578	.7720	.7714	1.12	1.31	

Table 5-5 (Continued)

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2	
	136.2	.17200	.18970	.8510	.8688	1.27	1.79	
	204.2	.24900	.26653	.8730	.9032	1.43	2.43	
	272.3	.32200	.33004	.8820	.9221	1.61	3.26	
	408.4	.46100	.42713	.8840	.9436	2.00	5.76	*
477.6	34.0	.03200	.03530	.3100	.2987	1.04	1.08	
	68.1	.10300	.10769	.5680	.5695	1.12	1.28	
	136.2	.22400	.22835	.7000	.7495	1.29	1.79	
	204.2	.34100	.32335	.7360	.8231	1.47	2.47	
	273.5	.44800	.39786	.7490	.8611	1.69	3.37	*
	335.6	.55500	.61579	.7470	.9015	1.41	6.21	*

RMS deviation in x_1 = 0.0099

*Indicates data point ignored in fitting and calculation
of average error.

Table 5-6

Hydrogen (1)-Water (2), K_{12} = 0.0

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
273.2	25.0	.00040	.00045	.0	.9997	1.02	1.02
	50.0	.00090	.00090	.0	.9999	1.05	1.04
	100.0	.00170	.00177	.0	.9999	1.10	1.08
	200.0	.00330	.00342	.0	.9999	1.22	1.17
	400.0	.00640	.00646	.0	.9999	1.47	1.38
	600.0	.00930	.00920	.0	.9999	1.78	1.61
	800.0	.01190	.01171	.0	.9999	2.14	1.88
	1000.0	.01430	.01401	.0	.9999	2.57	2.20
293.2	25.0	.00040	.00039	.0	.9990	1.02	1.02
	50.0	.00070	.00076	.0	.9995	1.05	1.04
	100.0	.00140	.00151	.0	.9997	1.09	1.08
	200.0	.00280	.00294	.0	.9998	1.19	1.16
	400.0	.00540	.00560	.0	.9999	1.42	1.35
	600.0	.00790	.00806	.0	.9999	1.69	1.56
	800.0	.01020	.01036	.0	.9999	2.00	1.80
	1000.0	.01240	.01250	.0	.9999	2.36	2.09
313.2	25.0	.00030	.00035	.0	.9970	1.02	1.02
	50.0	.00070	.00069	.0	.9984	1.04	1.04
	100.0	.00130	.00136	.0	.9992	1.09	1.07
	200.0	.00260	.00267	.0	.9995	1.18	1.15
	400.0	.00500	.00512	.0	.9997	1.39	1.32
	600.0	.00730	.00740	.0	.9998	1.63	1.52
	800.0	.00950	.00954	.0	.9998	1.91	1.74
	1000.0	.01160	.01157	.0	.9999	2.23	2.00
333.2	25.0	.00030	.00033	.0	.9919	1.02	1.02
	50.0	.00070	.00066	.0	.9958	1.04	1.03
	100.0	.00130	.00131	.0	.9978	1.08	1.07
	200.0	.00250	.00257	.0	.9988	1.17	1.14
	400.0	.00490	.00495	.0	.9993	1.37	1.30
	600.0	.00720	.00717	.0	.9995	1.59	1.49
	800.0	.00940	.00928	.0	.9996	1.84	1.69
	1000.0	.01140	.01128	.0	.9996	2.13	1.93
353.2	25.0	.00030	.00033	.0	.9808	1.02	1.02
	50.0	.00070	.00067	.0	.9901	1.04	1.03
	100.0	.00130	.00133	.0	.9948	1.08	1.07
	200.0	.00260	.00262	.0	.9972	1.16	1.14
	400.0	.00510	.00507	.0	.9984	1.34	1.29
	600.0	.00740	.00737	.0	.9988	1.55	1.46
	800.0	.00970	.00955	.0	.9990	1.79	1.65

Table 5-6 (Continued)

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
.	1000.0	.01180	.01163	.0	.9992	2.05	1.87
373.2	25.0	.00040	.00035	.0	.9590	1.02	1.01
	50.0	.00070	.00072	.0	.9790	1.04	1.03
	100.0	.00140	.00144	.0	.9891	1.07	1.06
	200.0	.00280	.00284	.0	.9941	1.15	1.13
	400.0	.00550	.00552	.0	.9967	1.32	1.27
	600.0	.00800	.00804	.0	.9976	1.52	1.44
	800.0	.01030	.01044	.0	.9981	1.74	1.62
	1000.0	.01250	.01272	.0	.9984	1.98	1.82

RMS deviation in x_1 = 0.001

Table 5-7

Hydrogen (1)-Ammonia (2), K_{12} = 0.0

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
273.2	50.0	.00250	.00243	.0	.9073	1.05	1.06
	100.0	.00510	.00495	.0	.9482	1.11	1.12
	200.0	.00990	.00967	.0	.9686	1.24	1.26
	400.0	.01820	.01800	.0	.9785	1.54	1.59
	600.0	.02520	.02523	.0	.9818	1.90	2.00
	800.0	.03120	.03162	.0	.9834	2.33	2.50
	1000.0	.03640	.03734	.0	.9844	2.83	3.13
298.2	50.0	.00340	.00328	.0	.7783	1.04	1.05
	100.0	.00740	.00719	.0	.8773	1.10	1.11
	200.0	.01500	.01448	.0	.9270	1.23	1.24
	400.0	.02820	.02740	.0	.9516	1.51	1.55
	600.0	.03920	.03859	.0	.9597	1.84	1.94
	800.0	.04890	.04849	.0	.9639	2.23	2.40
	1000.0	.05680	.05736	.0	.9664	2.69	2.97
323.2	50.0	.00390	.00376	.0	.5513	1.03	1.03
	100.0	.01010	.00982	.0	.7504	1.09	1.09
	200.0	.02180	.02113	.0	.8525	1.21	1.22
	400.0	.04240	.04110	.0	.9039	1.47	1.53
	600.0	.05970	.05837	.0	.9211	1.79	1.89
	800.0	.07410	.07364	.0	.9299	2.15	2.33
	1000.0	.08670	.08736	.0	.9352	2.57	2.87
348.2	100.0	.01230	.01208	.0	.5538	1.07	1.08
	200.0	.03050	.02981	.0	.7336	1.17	1.20
	400.0	.06290	.06136	.0	.8271	1.42	1.50
	600.0	.09060	.08893	.0	.8595	1.70	1.86
	800.0	.11390	.11365	.0	.8756	2.02	2.30
	1000.0	.13380	.13633	.0	.8855	2.39	2.83
373.2	100.0	.01180	.01120	.0	.2830	1.03	1.05
	200.0	.04160	.03944	.0	.5545	1.13	1.18
	400.0	.09650	.09107	.0	.7080	1.33	1.49
	600.0	.14550	.13848	.0	.7602	1.55	1.87
	800.0	.18830	.18448	.0	.7889	1.78	2.34
	1000.0	.22780	.23291	.0	.8062	2.00	2.95

RMS deviation in x_1 = 0.0021

y_1^{exp} = 0 indicates no vapor phase composition available

Table 5-8

Hydrogen (1)-Methanol (2), $K_{12} = 0.0$

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
294.2	76.0	.01150	.01153	.0	.9983	1.06	1.13
	178.0	.02710	.02681	.0	.9993	1.14	1.34
	179.0	.02740	.02696	.0	.9993	1.14	1.35
	272.0	.04070	.04076	.0	.9996	1.22	1.57
	284.0	.04240	.04254	.0	.9996	1.23	1.60
363.2	71.0	.01560	.01469	.0	.9633	1.05	1.11
	74.0	.01650	.01532	.0	.9648	1.05	1.11
	134.0	.02860	.02802	.0	.9811	1.10	1.22
	186.0	.04010	.03894	.0	.9868	1.14	1.31
	284.0	.05920	.05947	.0	.9918	1.21	1.52
	300.0	.06200	.06284	.0	.9923	1.22	1.55
413.2	78.0	.02240	.01903	.8900	.8446	1.04	1.10
	196.0	.05400	.05227	.9530	.9412	1.12	1.30
	281.0	.07610	.07659	.9650	.9610	1.17	1.46
	300.0	.08094	.08213	.9700	.9638	1.18	1.50

RMS deviation in x_1 = 0.0012

y_1^{exp} = 0 indicates no vapor phase composition available

Table 5-9

Carbon monoxide (1)-Methanol (2), $K_{12} = \sim 0.10$

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2	
298.2	60.0	.01910	.02098	.0	.9970	0.98	1.11	
	67.0	.02170	.02338	.0	.9972	0.98	1.12	
	110.0	.03580	.03771	.0	.9982	0.98	1.20	
	180.0	.05560	.05882	.0	.9987	0.99	1.36	
	186.0	.05590	.06044	.0	.9988	0.99	1.37	
	241.0	.07570	.07313	.0	.9989	1.03	1.51	
	243.0	.07710	.07350	.0	.9989	1.03	1.52	
363.2	50.0	.02220	.01740	.0	.9438	1.02	1.07	
	100.0	.03910	.03471	.0	.9703	1.04	1.16	
	150.0	.05270	.05061	.0	.9790	1.08	1.25	
	200.0	.06450	.06471	.0	.9832	1.13	1.35	
	250.0	.07390	.07662	.0	.9857	1.19	1.45	
	300.0	.08150	.08609	.0	.9873	1.27	1.57	*
413.2	86.0	.03820	.03623	.8870	.8480	1.01	1.11	
	90.0	.04030	.03814	.8930	.8542	1.01	1.12	
	145.0	.06150	.06408	.9250	.9039	1.03	1.22	
	291.0	.09100	.12482	.9630	.9453	1.12	1.52	*

RMS deviation in x_1 = 0.0029

y_1^{exp} = 0 indicates no vapor phase composition available

* Indicates data point ignored in fitting and calculation of average error.

Table 5-10

Nitrogen (1)-Ammonia (2), $K_{12} = 0.0$

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2	
273.2	50.0	.00310	.00287	.0	.9115	1.07	1.06	
	100.0	.00600	.00538	.0	.9533	1.17	1.12	
	200.0	.01030	.00914	.0	.9746	1.38	1.26	
	300.0	.01330	.01194	.0	.9819	1.64	1.42	
	400.0	.01550	.01422	.0	.9858	1.95	1.59	
	600.0	.01860	.01791	.0	.9898	2.74	2.00	
	800.0	.02090	.02090	.0	.9920	3.82	2.50	
	1000.0	.02210	.02347	.0	.9933	5.27	3.12	
293.2	50.0	.00410	.00392	.0	.8152	1.06	1.05	
	100.0	.00840	.00789	.0	.9025	1.14	1.11	
	200.0	.01530	.01407	.0	.9473	1.34	1.25	
	300.0	.02050	.01879	.0	.9628	1.58	1.40	
	400.0	.02450	.02265	.0	.9709	1.87	1.56	
	600.0	.02980	.02888	.0	.9794	2.58	1.95	
	800.0	.03320	.03393	.0	.9838	3.54	2.42	
	1000.0	.03560	.03825	.0	.9866	4.81	2.99	
313.2	50.0	.00480	.00490	.0	.6616	1.05	1.04	
	100.0	.01130	.01112	.0	.8203	1.12	1.10	
	200.0	.02240	.02116	.0	.9032	1.30	1.23	
	300.0	.03130	.02901	.0	.9322	1.51	1.38	
	400.0	.03810	.03549	.0	.9472	1.77	1.54	
	600.0	.04730	.04593	.0	.9629	2.42	1.91	
	800.0	.05350	.05436	.0	.9711	3.27	2.36	
	1000.0	.05720	.06156	.0	.9761	4.39	2.90	
333.2	50.0	.00480	.00511	.0	.4373	1.03	1.03	
	100.0	.01430	.01481	.0	.6957	1.09	1.09	
	200.0	.03170	.03115	.0	.8349	1.24	1.22	
	300.0	.04630	.04436	.0	.8851	1.42	1.36	
	400.0	.05880	.05540	.0	.9112	1.65	1.52	
	600.0	.07770	.07328	.0	.9383	2.21	1.88	
	800.0	.08850	.08772	.0	.9523	2.95	2.32	
	1000.0	.09540	.10010	.0	.9609	3.91	2.85	
353.2	50.0	.00200	.00274	.0	.1410	1.01	1.01	
	100.0	.01580	.01777	.0	.5149	1.05	1.07	
	200.0	.04400	.04454	.0	.7322	1.16	1.20	
	300.0	.07050	.06720	.0	.8150	1.31	1.35	*
	400.0	.09460	.08648	.0	.8578	1.50	1.51	*
373.2	100.0	.01530	.01731	.0	.2947	1.01	1.05	*

RMS deviation in x_1 = 0.0023

y_1^{exp} = 0 indicates no vapor composition available

*Indicates data point ignored in fitting and calculation of
average error.

Table 5-11

Ethane (1)–Water (2), K_{12} = 0.0

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
310.9	13.6	.00031	.00029	.0	.9951	1.03	1.01
	38.7	.00065	.00065	.0	.9982	1.08	1.03
	131.0	.00082	.00083	.0	.9992	1.32	1.10
	212.1	.00089	.00089	.0	.9993	1.59	1.16
	342.8	.00102	.00096	.0	.9994	2.12	1.27
	430.9	.00111	.00100	.0	.9995	2.57	1.35
	643.6	.00113	.00106	.0	.9996	4.08	1.57
344.3	13.3	.00015	.00020	.0	.9751	1.02	1.01
	34.9	.00042	.00046	.0	.9901	1.06	1.02
	53.4	.00057	.00062	.0	.9934	1.10	1.04
	135.1	.00079	.00085	.0	.9969	1.30	1.09
	222.9	.00089	.00095	.0	.9974	1.54	1.16
	332.5	.00101	.00104	.0	.9978	1.91	1.24
	441.5	.00108	.00112	.0	.9981	2.36	1.33
	656.9	.00117	.00123	.0	.9984	3.58	1.53
377.6	14.4	.00013	.00018	.0	.9169	1.02	1.01
	37.3	.00039	.00043	.0	.9667	1.06	1.02
	76.2	.00066	.00072	.0	.9830	1.14	1.05
	133.8	.00094	.00093	.0	.9893	1.26	1.08
	172.6	.00104	.00101	.0	.9908	1.35	1.11
	235.2	.00113	.00111	.0	.9921	1.51	1.15
	477.2	.00133	.00138	.0	.9944	2.33	1.33
	676.3	.00151	.00153	.0	.9954	3.30	1.50
410.9	14.3	.00016	.00016	.0	.7612	1.02	1.01
	37.9	.00046	.00045	.0	.9070	1.06	1.02
	66.6	.00080	.00073	.0	.9451	1.11	1.04
	143.3	.00121	.00117	.0	.9717	1.26	1.08
	244.0	.00153	.00146	.0	.9799	1.49	1.15
	343.4	.00170	.00166	.0	.9833	1.75	1.21
	440.1	.00187	.00182	.0	.9854	2.05	1.28
	665.4	.00200	.00211	.0	.9886	2.96	1.45
444.3	15.4	.00014	.00014	.0	.4707	1.01	1.00
	36.0	.00050	.00050	.0	.7675	1.04	1.02
	67.5	.00104	.00094	.0	.8713	1.09	1.03
	135.1	.00167	.00160	.0	.9303	1.21	1.07
	247.8	.00232	.00220	.0	.9553	1.45	1.14
	342.8	.00252	.00254	.0	.9634	1.68	1.20
	451.3	.00279	.00286	.0	.9690	1.98	1.27
	635.5	.00320	.00329	.0	.9749	2.63	1.40

RMS deviation in x_1 = 0.00005

y_1^{exp} = 0 indicates no vapor composition data available

Table 5-12

Methane (1)-Water (2), $K_{12} = 0.0$

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
298.2	23.2	.00050	.00056	.0	.9985	1.03	1.02
	44.9	.00100	.00101	.0	.9991	1.06	1.03
	87.8	.00168	.00172	.0	.9994	1.13	1.07
	169.8	.00258	.00261	.0	.9995	1.28	1.13
	239.3	.00311	.00309	.0	.9996	1.43	1.19
	327.4	.00366	.00356	.0	.9996	1.65	1.27
	438.4	.00417	.00403	.0	.9996	1.97	1.38
	633.1	.00445	.00467	.0	.9996	2.69	1.59
310.9	22.5	.00044	.00047	.0	.9968	1.03	1.02
	45.2	.00084	.00089	.0	.9982	1.06	1.03
	86.5	.00144	.00151	.0	.9989	1.13	1.06
	175.3	.00229	.00241	.0	.9991	1.28	1.13
	240.6	.00276	.00285	.0	.9992	1.42	1.19
	334.2	.00333	.00335	.0	.9992	1.63	1.27
	444.2	.00391	.00382	.0	.9993	1.93	1.37
	673.6	.00465	.00459	.0	.9993	2.73	1.60
344.3	22.5	.00034	.00036	.0	.9844	1.03	1.01
	44.9	.00063	.00069	.0	.9915	1.06	1.03
	89.4	.00118	.00125	.0	.9949	1.12	1.06
	173.9	.00192	.00204	.0	.9964	1.26	1.12
	240.6	.00238	.00250	.0	.9968	1.37	1.17
	335.3	.00277	.00302	.0	.9971	1.56	1.24
	444.2	.00342	.00352	.0	.9973	1.81	1.33
	671.6	.00424	.00435	.0	.9976	2.46	1.54
377.6	22.7	.00032	.00033	.0	.9449	1.03	1.01
	44.4	.00061	.00063	.0	.9700	1.05	1.03
	89.2	.00119	.00118	.0	.9829	1.11	1.05
	172.6	.00198	.00199	.0	.9887	1.23	1.11
	243.0	.00251	.00252	.0	.9903	1.35	1.16
	338.0	.00314	.00311	.0	.9914	1.52	1.23
	444.2	.00361	.00367	.0	.9922	1.73	1.31
	672.2	.00451	.00464	.0	.9933	2.29	1.50
410.9	22.9	.00033	.00033	.0	.8460	1.02	1.01
	44.5	.00067	.00067	.0	.9165	1.05	1.02
	89.2	.00133	.00130	.0	.9533	1.10	1.05
	162.8	.00235	.00216	.0	.9694	1.20	1.10
	242.0	.00301	.00292	.0	.9755	1.32	1.15
	338.7	.00380	.00368	.0	.9790	1.47	1.21
	444.2	.00449	.00439	.0	.9813	1.66	1.29

Table 5-12 (Continued)

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
	669.5	.00574	.00566	.0	.9842	2.15	1.46
444.3	22.0	.00032	.00031	.0	.6231	1.01	1.01
	45.1	.00079	.00079	.0	.8067	1.04	1.02
	92.6	.00173	.00169	.0	.8959	1.09	1.05
	175.6	.00302	.00287	.0	.8892	1.20	1.10
	243.7	.00383	.00394	.0	.9468	1.29	1.14
	343.4	.00487	.00509	.0	.9557	1.44	1.20
	444.2	.00595	.00610	.0	.9608	1.60	1.27
	630.4	.00775	.00768	.0	.9667	1.96	1.40

RMS deviation in x_1 = 0.00009

y_1^{exp} = 0 indicates no vapor composition data available

Table 5-13

Carbon dioxide (1)-Water (2), $K_{12} = -0.20$

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
273.2	1.0	.00145	.00147	.0	.9939	1.02	1.00
	5.0	.00677	.00673	.0	.9987	1.09	1.00
	10.0	.01269	.01216	.0	.9993	1.18	1.01
	20.0	.02097	.02046	.0	.9996	1.31	1.01
	30.0	.02642	.02644	.0	.9997	1.43	1.02
	34.0	.02823	.02835	.0	.9997	1.47	1.02
278.2	1.0	.00183	.00117	.0	.9913	1.02	1.00
	10.0	.01056	.01001	.0	.9991	1.14	1.01
	20.0	.01810	.01717	.0	.9995	1.26	1.01
	38.0	.02536	.02573	.0	.9996	1.42	1.03
283.2	1.0	.00095	.00095	.0	.9878	1.01	1.00
	5.0	.00460	.00450	.0	.9975	1.06	1.00
	10.0	.00854	.00833	.0	.9987	1.12	1.01
	20.0	.01535	.01452	.0	.9993	1.21	1.01
	38.0	.02191	.02219	.0	.9995	1.35	1.03
285.6	1.0	.00081	.00087	.0	.9857	1.01	1.00
	5.0	.00413	.00412	.0	.9970	1.06	1.00
	10.0	.00771	.00766	.0	.9984	1.11	1.01
	20.0	.01360	.01345	.0	.9991	1.20	1.01
	30.0	.01838	.01790	.0	.9994	1.27	1.02
	45.0	.02208	.02272	.0	.9995	1.37	1.03
288.2	1.0	.00078	.00079	.0	.9831	1.01	1.00
	5.0	.00368	.00375	.0	.9965	1.05	1.00
	10.0	.00693	.00702	.0	.9982	1.10	1.01
	20.0	.01211	.01240	.0	.9990	1.18	1.01
	30.0	.01610	.01660	.0	.9992	1.25	1.02
	45.0	.02020	.01919	.0	.8850	1.31	1.03
298.2	1.0	.00061	.00056	.0	.9684	1.01	1.00
	20.0	.00976	.00937	.0	.9981	1.13	1.01
	45.0	.01645	.01666	.0	.9989	1.26	1.03

RMS deviation in x_1 = 0.0004

y_1^{exp} = 0 indicates no vapor composition data available

Table 5-14

Methane (1)-Propane (2), K_{12} = 0.015

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
310.9	13.6	.00490	.00451	.0521	.0456	1.00	1.00
	20.4	.04600	.04496	.3255	.3117	0.99	1.03
	34.0	.12350	.12403	.5209	.5268	0.98	1.09
	51.0	.22160	.22110	.6210	.6260	0.96	1.18
	68.1	.32710	.32083	.6635	.6636	0.92	1.30
	81.7	.42260	.41296	.6779	.6742	0.87	1.45
	91.9	.56100	.55588	.6087	.6829	0.73	1.86
344.3	27.2	.00630	.00610	.0276	.0275	1.00	1.00
	34.0	.04330	.04444	.1550	.1606	0.98	1.03
	40.8	.08130	.08372	.2392	.2492	0.96	1.06
	47.6	.11990	.12496	.2983	.3101	0.93	1.10
	54.4	.16180	.17165	.3414	.3546	0.89	1.15
	61.2	.20810	.23501	.3656	.3741	0.78	1.23

RMS deviation in x_1 = 0.0088

Table 5-15

Methane (1)-n-Butane (2), K_{12} = 0.040

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2	
310.9	4.1	.00290	.00316	.1335	.1308	1.00	1.00	
	6.8	.01750	.01798	.4596	.4552	1.00	1.01	
	13.6	.05300	.05438	.7027	.7037	1.00	1.04	
	27.2	.12160	.12442	.8239	.8268	1.00	1.11	
	54.4	.25400	.25587	.8774	.8807	0.99	1.26	
	81.7	.38100	.38116	.8798	.8887	0.97	1.46	
	108.9	.51680	.51375	.9570	.8849	0.93	1.80	*
327.6	6.8	.00640	.00677	.1791	.1739	1.00	1.01	
	13.6	.04040	.04127	.5531	.5481	1.00	1.03	
	27.2	.10600	.10777	.7390	.7379	1.00	1.09	
	54.4	.23180	.23298	.8193	.8247	1.00	1.24	
	81.7	.35560	.35244	.8283	.8422	0.99	1.43	
	108.9	.48880	.47699	.8042	.8422	0.95	1.72	*
344.3	10.2	.00900	.00981	.1722	.1691	1.00	1.01	
	20.4	.05730	.05874	.5318	.5293	1.00	1.05	
	27.2	.08850	.09055	.6233	.6206	1.00	1.08	
	54.4	.21190	.21240	.7451	.7507	1.00	1.22	
	81.7	.33280	.33019	.7594	.7811	0.99	1.41	
	108.9	.46960	.45611	.7285	.7877	0.95	1.69	*
360.9	13.6	.00790	.00824	.1110	.1035	1.00	1.01	
	20.4	.03870	.04002	.3626	.3470	1.00	1.04	
	27.2	.06950	.07130	.4848	.4723	1.00	1.06	
	54.4	.19160	.19257	.6529	.6537	0.99	1.20	
	81.7	.31540	.31393	.6745	.6989	0.97	1.39	
	108.8	.46850	.46101	.6265	.7175	0.90	1.73	*
377.6	20.4	.01750	.01849	.1599	.1479	1.00	1.02	
	27.2	.04759	.04968	.3241	.3057	1.00	1.05	
	40.8	.10940	.11128	.4799	.4642	0.99	1.11	
	54.4	.17220	.17284	.5428	.5405	0.98	1.19	
	68.1	.23560	.23616	.5630	.5801	0.96	1.27	
	81.7	.30110	.30529	.5613	.6019	0.93	1.39	
	95.3	.38190	.39675	.5370	.6218	0.85	1.58	*
394.3	27.2	.02170	.02240	.1418	.1206	1.00	1.02	
	34.0	.05300	.05344	.2650	.2328	0.99	1.05	
	40.8	.08500	.08464	.3411	.3077	0.98	1.09	
	54.4	.15190	.14834	.4147	.3960	0.96	1.16	
	68.1	.21920	.21741	.4327	.4361	0.92	1.26	
	81.7	.30200	.31300	.4101	.4631	0.82	1.43	*

RMS deviation in x_1 = 0.0017

*
Indicates data point ignored in fitting and calculation of average error.

Table 5-16

Methane (1)-n-Pentane (2), K_{12} = 0.05

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2
310.9	1.4	.00150	.00155	.2090	.2079	1.00	1.00
	4.1	.01540	.01586	.7160	.7230	1.00	1.01
	6.8	.02880	.02997	.8178	.8273	1.00	1.03
	27.2	.12820	.13008	.9323	.9429	1.02	1.13
	68.1	.30770	.30587	.9470	.9595	1.03	1.40
	102.1	.43900	.43826	.9410	.9568	1.03	1.72
	136.1	.57880	.57985	.9204	.9515	1.00	2.27
344.3	4.1	.00537	.00575	.2805	.2725	1.00	1.01
	6.8	.01760	.01878	.5524	.5447	1.00	1.02
	13.6	.04801	.05069	.7568	.7528	1.01	1.05
	27.2	.10700	.11169	.8485	.8563	1.02	1.12
	68.1	.27430	.27725	.8937	.9102	1.05	1.36
	102.1	.40020	.40413	.8875	.9142	1.06	1.65
	136.1	.54600	.54068	.8558	.9131	1.03	2.13
377.6	6.8	.00150	.00155	.0458	.0433	1.00	1.00
	13.6	.03010	.03199	.4722	.4705	1.01	1.03
	27.2	.08696	.09055	.6846	.6943	1.02	1.10
	40.8	.14350	.14652	.7566	.7675	1.03	1.17
	68.1	.25090	.25289	.7981	.8205	1.04	1.34
	102.1	.38170	.38360	.7940	.8391	1.04	1.62
410.9	13.6	.00430	.00426	.0578	.0553	1.00	1.00
	20.4	.03370	.03336	.3051	.3031	1.01	1.04
	27.2	.06231	.06197	.4289	.4337	1.01	1.07
	40.8	.11780	.11784	.5532	.5663	1.02	1.14
	68.1	.22970	.22717	.6429	.6667	1.02	1.31

RMS deviation in x_1 = 0.0023

Table 5-17

Methane (1)-n-Decane (2), K_{12} = 0.08

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2	
310.9	2.7	.01400	.01198	.9979	.9980	1.00	1.02	
	6.8	.03430	.02966	.9990	.9991	1.01	1.05	
	27.2	.12510	.11300	.9994	.9996	1.02	1.24	
	68.1	.26790	.26078	.9993	.9996	1.04	1.73	
	136.1	.44690	.44980	.9981	.9317	1.03	3.20	
	204.1	.58270	.57066	.9942	.8238	1.02	6.40	*
	272.2	.68700	.60369	.9837	.7423	1.13	11.93	*
344.3	2.7	.01240	.01163	.9891	.9895	1.01	1.02	
	6.8	.03070	.02886	.9950	.9955	1.01	1.05	
	27.2	.11380	.10907	.9980	.9984	1.05	1.22	
	68.1	.24960	.24501	.9980	.9987	1.12	1.65	
	136.1	.42340	.42741	.9963	.9983	1.22	2.77	
	204.1	.55930	.62684	.9915	.9979	1.20	5.42	*
	272.2	.67960	.68604	.9779	.9017	1.31	9.96	*
377.6	2.7	.01090	.01112	.9570	.9585	1.01	1.02	
	6.8	.02750	.02812	.9811	.9824	1.02	1.05	
	27.2	.10440	.10713	.9931	.9941	1.06	1.21	
	68.1	.23520	.24043	.9947	.9960	1.15	1.60	
	136.1	.40910	.41456	.9921	.9959	1.29	2.57	
	204.1	.54620	.56210	.9842	.9957	1.40	4.32	*
	272.2	.67820	.73097	.9657	.9706	1.40	9.21	*
410.9	2.7	.00900	.01003	.8654	.8673	1.01	1.02	
	6.8	.02450	.02693	.9411	.9444	1.02	1.04	
	27.2	.09740	.10561	.9798	.9826	1.07	1.19	
	68.1	.22560	.23888	.9870	.9895	1.17	1.56	
	136.1	.40280	.41337	.9845	.9909	1.33	2.45	
	204.1	.54760	.55783	.9715	.9913	1.46	3.95	*
	272.2	.69120	.75450	.9430	.9899	1.44	8.63	*
444.3	2.7	.00660	.00761	.6493	.6480	1.00	1.01	
	6.8	.02160	.02454	.8489	.8528	1.02	1.04	
	27.2	.09320	.10356	.9511	.9558	1.07	1.18	
	68.1	.22130	.23830	.9693	.9755	1.17	1.53	
	136.1	.40250	.41706	.9656	.9812	1.33	2.36	*
	204.1	.56070	.56887	.9477	.9836	1.47	3.79	*
	272.2	.73580	.77324	.8823	.9770	1.44	8.66	*
477.6	2.7	.00230	.00254	.2120	.2028	1.00	1.00	
	6.8	.01780	.01963	.6662	.6587	1.01	1.03	
	27.2	.09260	.09966	.8851	.8990	1.07	1.17	

Table 5-17 (Continued)

T,K	P,atm	x_1,exp	x_1,calc	y_1,exp	y_1,calc	γ_1	γ_2	
	68.1	.22580	.23738	.9358	.9468	1.17	1.51	
	136.1	.41190	.42492	.9351	.9622	1.32	2.34	*
	204.1	.59120	.60383	.9030	.9694	1.41	3.95	*
510.9	5.4	.00450	.00442	.1830	.1623	1.00	1.01	
	13.6	.03850	.03839	.6409	.6189	1.02	1.06	
	27.2	.09370	.09193	.7928	.7865	1.06	1.15	
	54.4	.19320	.18939	.8698	.8726	1.12	1.37	
	102.1	.33740	.33837	.8873	.9126	1.23	1.86	
	136.1	.42800	.43725	.8815	.9254	1.28	2.35	*
	170.1	.53790	.54908	.8534	.9353	1.29	3.15	*

RMS deviation in x_1 = 0.0073

*
Indicates data point ignored in fitting and calculation
of average error.

Table 5-18

Summary of Correlations of Binary Gas-Solvent Systems

$$\ln H_{12} = a_0 + a_1 \times 10^{-2} T + a_2 \times 10^{-5} T^2 \qquad H_{12} - \text{atm}; \ T - K$$

	K_{12}	a_0	a_1	a_2	Temp. range K	Maximum Mole Fraction	Maximum Pressure, atm	Ref.	Vapor Phase Eqn.*
1. Carbon monoxide-benzene	0.10	4.0903	1.5908	-2.2424	433-533	0.10	103	6	a
2. Carbon monoxide-n-octane	0.21	4.0704	1.2509	-1.7843	463-533	0.11	51	6	a
3. Hydrogen-benzene	0.0	5.4002	1.4278	-2.2992	433-533	0.13	176	12	a
4. Hydrogen-n-octane	0.0	1.1254	2.7622	-3.5184	463-533	0.25	148	6	a
5. Hydrogen-n-hexane	0.0	5.8573	0.9446	-1.9094	277-477	0.34	544	13	a
6. Hydrogen-water	0.0	2.5056	5.1736	-7.6795	273-373	.014	1000	14	b
7. Hydrogen-ammonia	0.0	14.4187	-1.6303	-0.2002	273-373	0.23	1000	15	b
8. Hydrogen-methanol	0.0	9.9024	-0.2872	-0.3166	294-413	0.08	300	16	c
9. Carbon monoxide-methanol	-0.10	4.0725	2.4266	-3.7888	298-413	0.08	250	16	c
10. Nitrogen-ammonia	0.0	15.4483	-2.3280	0.6459	273-373	0.110	1000	17	b
11. Ethane-water	0.0	-2.2676	6.9855	-9.0946	311-444	0.003	676	18	b
12. Methane-water	0.0	-0.1832	5.9635	-7.9178	298-444	0.008	670	19	b
13. Carbon dioxide-water	-0.20	-32.5888	23.9184	-35.1854	273-298	0.028	45	20	b
14. Methane-propane	0.015	5.00	0	0	311-344	0.56	92	21	a
15. Methane-n-butane	0.040	1.1393	2.2546	-3.0888	311-394	0.38	82	21	a
16. Methane-n-pentane	0.050	2.9802	1.1729	-1.4522	311-411	0.58	136	21	a
17. Methane-n-decane	0.080	4.8732	0.2771	-0.3304	311-511	0.45	136	21	a

*a - Modified Redlich-Kwong Equation (Reference 7)
 b - Perturbed Hard Sphere Equation (Reference 10)
 c - Hayden-O'Connell Second Virial Coefficient Correlation (Reference 8)

by Chueh and Prausnitz[7] for their binary parameter, but this is likely to be coincidence. All the binary interaction parameters behave in a reasonable fashion, i.e., are similar to values found in other correlations.[7]

The results obtained for systems containing polar solvents are very good. For all these binaries the assumption $K_{12} = 0$ has given accurate estimates of the liquid nonidealities. Figures 5-4 — 5-6 show some of the results obtained for these systems. For comparison we also show the predictions that would be obtained if Henry's law were assumed.

Table 5-13 shows the results obtained for the carbon dioxide-water system. It is not clear that the theory we propose can describe the complex interactions of this system. Further, or perhaps for the same reason, the system is the only one we have investigated where the composition nonidealities of the solute are greater than unity. Nevertheless, we have been able to correlate this data by using a negative binary parameter; the negative value can be justified as accounting for the association between carbon dioxide and water molecules. It should be noted that not all the data[20,22] are consistent. At T = 273K the data from the two sources agree, but at T = 298K Munjal's data[20] indicates a significantly higher activity coefficient than Houghton's data.[22] Our theory is closer to that of Munjal's since we can correlate it with a constant binary parameter but a correlation of Houghton's data over the same temperature range requires a temperature dependent binary parameter. To further complicate matters, our theory predicts that $\bar{V}_{CO_2}^{\infty}$ = 33 cc/g mole at
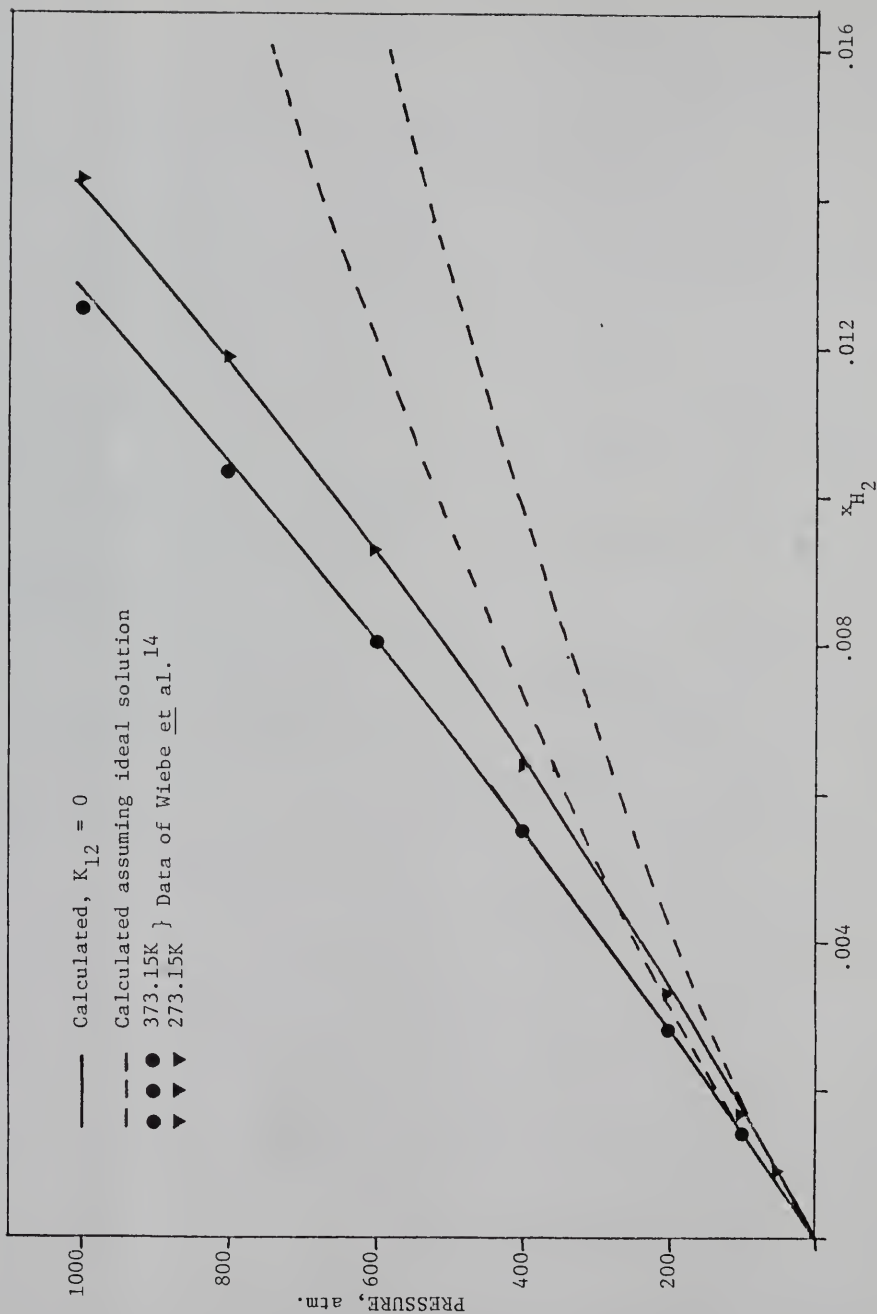
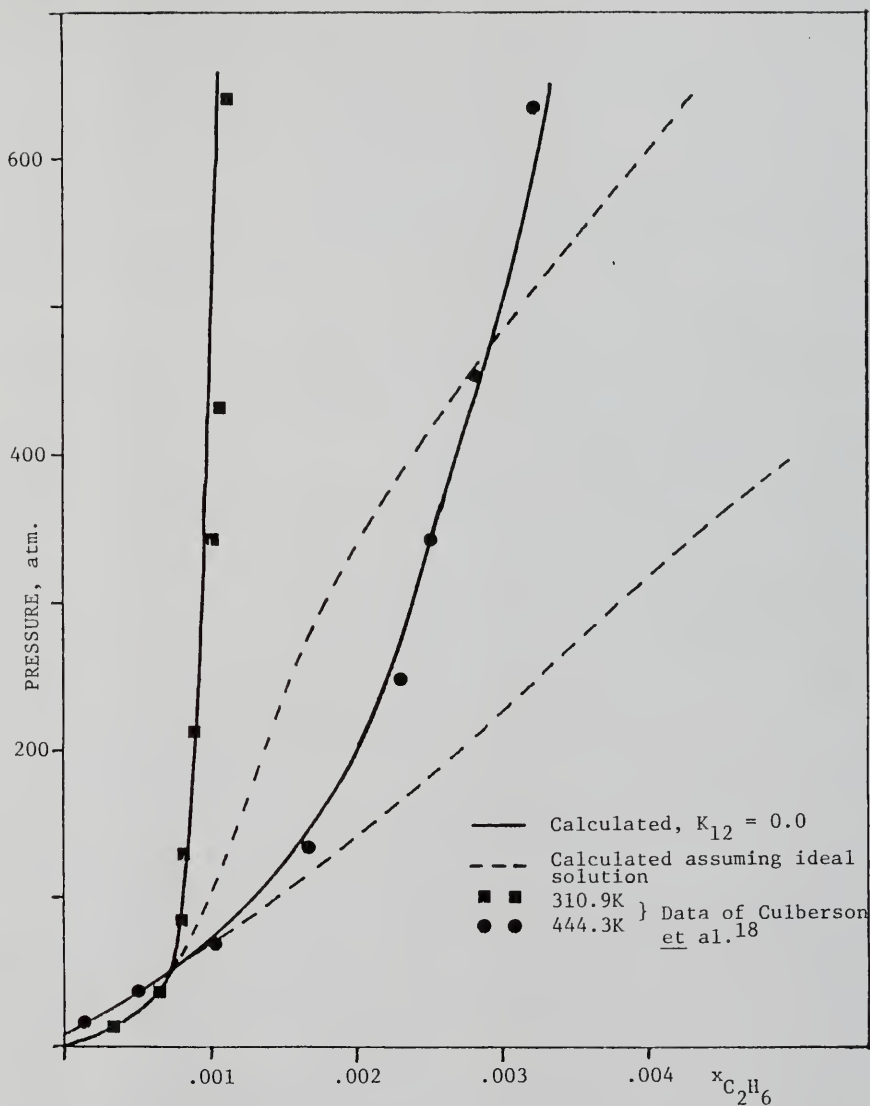Figure 5-4. Solubility of hydrogen in water
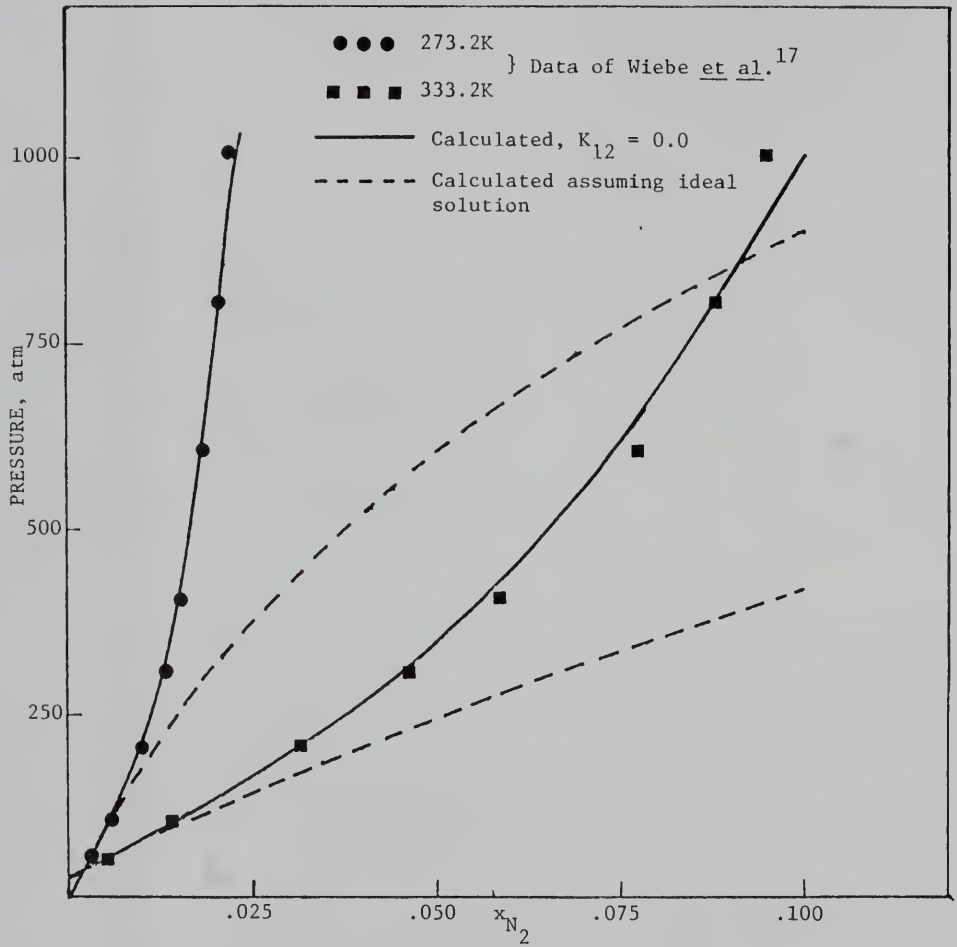
Figure 5-5. Solubility of ethane in water

Figure 5-6. Solubility of nitrogen in ammonia

298K, in close agreement with the value reported by Reid, Prausnitz and Sherwood[23] but low compared to the value of 37.6 cc/mole reported by Parkinson and de Nevers.[24] With all the experimental conflicts it is impossible to gauge whether the theory can describe the non-idealities of this system. Yet there is a set which we do describe well.

In summary, this method is a versatile way to correlate the vapor-liquid equilibrium of binary gas-solvent systems. It can correlate the data for nonpolar mixtures except at conditions approaching the critical point. The results for systems containing polar solvents are very good. We have been able to obtain adequate estimates of liquid nonidealities even with assuming $K_{12} = 0$, thus actually predicting binary data using only pure component compressibilities.

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CHAPTER 6
THERMODYNAMIC PROPERTIES OF BINARY GAS–SOLVENT
SYSTEMS; PREDICTION

In addition to correlating the nonideality of a solute in a solvent, Equation (2-25) can be used to relate Henry's constants of a solute in two different solvents. Denoting the solute by the subscript 1 and the solvents by subscripts 2 and 3, we can write

$$\ln \ (H_{13}/H_{12}) = \lim_{x_3 \to 1} \ \ln \left(\frac{f_1^L}{x_1}\right) - \lim_{x_2 \to 1} \ \ln \left(\frac{f_1^L}{x_1}\right) \qquad (6-1)$$

Equation (2-25) can now be used to evaluate the right side of Equation (6-1).

$$\ln \ (H_{13}/H_{12}) = \ln\left(\frac{\rho_3^o}{\rho_2^o}\right) - \int_0^1 \frac{1}{\rho(t)} \ [\rho_3^o C_{13}(\underline{\rho}(t)) - \rho_2^o C_{12}(\underline{\rho}(t))]dt \qquad (6-2)$$

where

$$\rho_1(t) = 0$$
$$\rho_2(t) = (1-t)\rho_2^o$$
$$\rho_3(t) = t\rho_3^o \qquad (6-3)$$
$$\rho(t) = \rho_1(t) + \rho_2(t) + \rho_3(t)$$

and ρ_2^o, ρ_3^o are the densities of the pure solvents.

Equation (6-2) represents an integration in number density space from pure component 2 as the reference state to pure component 3 as the

final state. The reference state is necessarily specified by the
temperature and the number density of all components, but as before
the final state can be specified either by a set of mole fractions
and a change in pressure or by a set of final number densities.
While we have adopted the former specification for previous calcula-
tions, here we use the latter. With the former choice we would first
have to use Equation (2-22) to solve for ρ_3^o and then use Equation (6-2)
to calculate the ratio of Henry's constants. The problem with this
procedure is that because the theory is not perfectly accurate,
invariably a different value of the ratio would be obtained if the
reference and final solvents are interchanged. This difficulty will
not arise if the density of the final state is specified as can be
seen from Equation (6-2).

The advantage of the number density specification is more
clearly seen if we add another solvent (which we denote by subscript
4) to the system. Because the integrals are independent of path
with this specification, we obtain

$$\frac{H_{14}}{H_{13}} = \left(\frac{H_{14}}{H_{12}}\right)\left(\frac{H_{12}}{H_{13}}\right) \tag{6-4}$$

Therefore, if the theory predicts the correct values for the
ratios H_{13}/H_{12} and H_{14}/H_{12} then it will necessarily predict the cor-
rect value for the ratio H_{14}/H_{13}.

This feature of the theory provides a way to ensure that Henry's
constants of any gas in all solvents are mutually consistent at a

particular value of temperature: we pick out a value--any value--for the binary parameter of the gas in any one (reference) solvent. Next the binary parameter of the gas in any other solvent can be found by ensuring that the theory predicts the correct value for the ratio of Henry's constants of the gas in this solvent and the reference solvent. Now Equation (6-4) ensures that Henry's constants in any two solvents are mutually consistent at this temperature.

But the above does not ensure that a constant value of the binary parameter will correctly follow the temperature variation of the ratio of Henry's constants. Further, the same binary parameter must also predict the deviation from ideality of the system at conditions removed from the reference state. This depends partly on the value of the gas-reference solvent binary parameter chosen but mainly on the ability of the theory to describe real fluid behavior. In this chapter we investigate ability of the theory to provide this level of description for a wide variety of systems including those containing polar solvents and coal oils.

6.1 Sensitivity to the Binary Parameter

It is of primary importance to determine the sensitivity of the ratio of Henry's constants to the binary parameter. The derivative of this quantity with respect to the binary parameter is

$$\frac{d\ln (H_{13}/H_{12})}{dK_{13}} = -\rho_3^o \int_0^1 \frac{1}{\rho(t)} \frac{d\ C_{13}(\rho(t))}{d\ K_{13}}\ dt \qquad (6\text{-}5)$$

Because of the way we have defined our binary parameter, the hard sphere direct correlation function integral is independent of K_{13} and we obtain a contribution only from the 2nd virial coefficient term. Thus,

$$\frac{d\ell n \ (H_{13}/H_{12})}{d \ K_{13}} = - \int_0^1 \frac{\rho_3^o}{\rho(t)} \ 2\rho(t) \ V_{13}^* \ \tilde{T}_{13} \ \frac{d\tilde{B}_2}{d\tilde{T}_{13}} \ dt$$

$$= - \ 2(\rho_3^o V_3^*) \ \left(\frac{V_{13}^*}{V_3^*}\right)\left(\tilde{T}_{13} \ \frac{d\tilde{B}_2}{d\tilde{T}_{13}}\right) \tag{6-6}$$

The simple form of Equation (6-6) is very convenient since it allows us to estimate the effect of various factors. We note the surprising but appealing result that the right hand side contains no quantities associated with the reference solvent. The first term in parentheses on the right side of the equation depends only on the reduced temperature of the solvent; it is lower as the temperature of the system increases and varies from approximately 1.6 at $T/T_{c_3} = 0.95$ to about 3 at $T/T_{c_3} = 0.5$. The second term is determined by the relative sizes of the solvent and solute (see the size mixing rule, Equation (3-17)); for the same solute it will be larger for smaller solvents. The contribution of the last term is shown in Table 6-1. It varies quite significantly with reduced temperature, but since component 1 is supercritical and component 3 is subcritical the value of $\tilde{T}_{13}$ normally encountered will be in the range $0.80 < \tilde{T} < 3.5$.

Table 6-2 shows the sensitivity of Henry's constant to the binary parameter for a wide variety of binary systems. It can be seen that for

Table 6-1

Temperature Derivative of the Reduced
Second Virial Coefficient

$\tilde{T}$	$\tilde{T}\,\dfrac{d\tilde{B}_2}{d\tilde{T}}$
0.50	11.36
0.60	6.10
0.70	4.21
0.80	3.25
0.90	2.64
1.0	2.23
1.5	1.21
2.0	0.82
3.5	0.32
5.0	0.19
10.0	0.05

Table 6-2

Sensitivity of Henry's Constant to the Binary Interaction Parameter

Component 1	Component 3	T^*_{13}, K	$\dfrac{V^*_{13}}{V^*_3}$	T, K	$\rho^o_3 V^*_3$	$\dfrac{d \ln H_{13}/H^*_{12}}{d \kappa_{13}}$
Carbon dioxide	Methanol	388.4	0.96	293.	2.27	17.5
Carbon dioxide	Benzene	408.0	0.62	293.	2.89	14.7
Argon	Water	257.1	1.29	293.	2.57	9.7
Methane	n-Butane	295.7	0.65	344.3	2.17	4.9
Methane	n-Decane	358.7	0.46	310.9	3.11	8.6
				344.3	2.99	6.6
				510.9	2.33	2.9
Hydrogen	n-Hexane	142.4	0.44	277.6	2.89	2.2
				477.6	1.84	0.8
Hydrogen	Water	130.1	1.07	273.	2.57	4.4
				444.	2.31	2.6
Methane	Water	290.2	1.50	273.	2.57	18.8
				444.	2.31	8.3
Nitrogen	n-Decane	290.9	0.45	310.9	3.11	5.91
				410.9	2.76	3.50
				510.9	2.33	2.10

*These derivatives are independent of the choice of component 2.

water as the solvent the sensitivity is high due to the small value of V_{13}^*. For carbon dioxide as the solute the value is high because of the large value of T_{13}^*. These represent extreme cases and it is unlikely that a value of K_{13} can be chosen in the absence of data that will predict Henry's constant for a supercritical species in such cases. (To achieve 1% accuracy in Henry's constant when the derivative is 10 requires an accuracy in K_{13} of 0.001.) However, for solutes like hydrogen, nitrogen and carbon monoxide in "large" solvents at high temperatures, the sensitivity is much less and prediction could be quite satisfactory.

6.2 Comparison with Experimental Data

In this section we show some comparisons of the calculation of gas solubility in one solvent using the solubility of the same gas in another solvent. The scheme we have adopted is approximately the same as the one used in Chapter 5; the only difference is that we estimate Henry's constant by the method described above. In this case we assume some value for the binary interaction parameter of the gas-reference solvent pair and fit on the value of the gas-solvent binary parameter to obtain the best agreement with the experimental solubility data. [The references for the experimental data are given in Table 5-18.]

Figure 6-1 shows a comparison of the solubility of carbon monoxide in n-octane estimated from the solubility of carbon monoxide in benzene. The excellent results are due to the quality of the data and to the similarity of the solvents. For one isotherm (463.15K) we also show the comparison between the predicted and calculated vapor
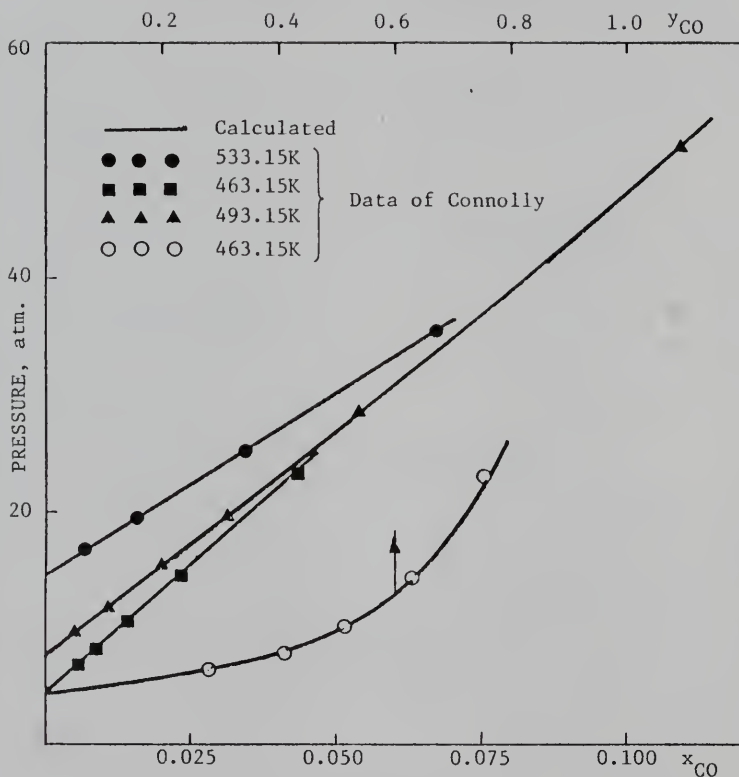
Figure 6-1. Solubility of carbon monoxide in n-octane calculated from the solubility of carbon monoxide in n-octane. $K_{CO-B_z} = 0.10$; $K_{CO-nC_8} = 0.219$. T = 463.15 isotherm also shows vapor composition

composition. The results are quite close to the experimental data but the mole fraction of the gas is slightly high. This, as we mentioned earlier, is a feature common to most systems we have investigated, but we are unable to account for its cause.

For the hydrogen systems we have chosen water as the reference solvent since we have obtained a very good fit of the data for this solvent and thus have a good estimate of Henry's constant over a wide temperature range. Further, the sensitivity of the results to k_{ij} are highest here. The binary constant for hydrogen-water that appears to work best for all systems is -0.24. This is very different from the value of 0.0 that we have listed in Table 5-18, but the predicted nonideality is quite insensitive to this value and Henry's constants obtained by fitting hydrogen-water data are practically unchanged. With this reference we have obtained good predictions of the solubility of hydrogen in methanol and ammonia which are similar to water and a reasonable prediction of the solubility in n-hexane, where the binary interaction parameter required is quite high (0.41). This last prediction is a severe test of the method since water and n-hexane are immiscible. The results are good because the Henry's constant ratio only accounts for the differences of environment of the infinitely dilute solute molecule. Thus the insensitivity of the calculation to the solvent-reference solvent interactions is substantially correct.

Figure 6-2 shows the comparison with the experimental data of the hydrogen-ammonia system obtained from hydrogen-water. We note that Henry's constant of hydrogen-ammonia changes by a factor of 6 over the
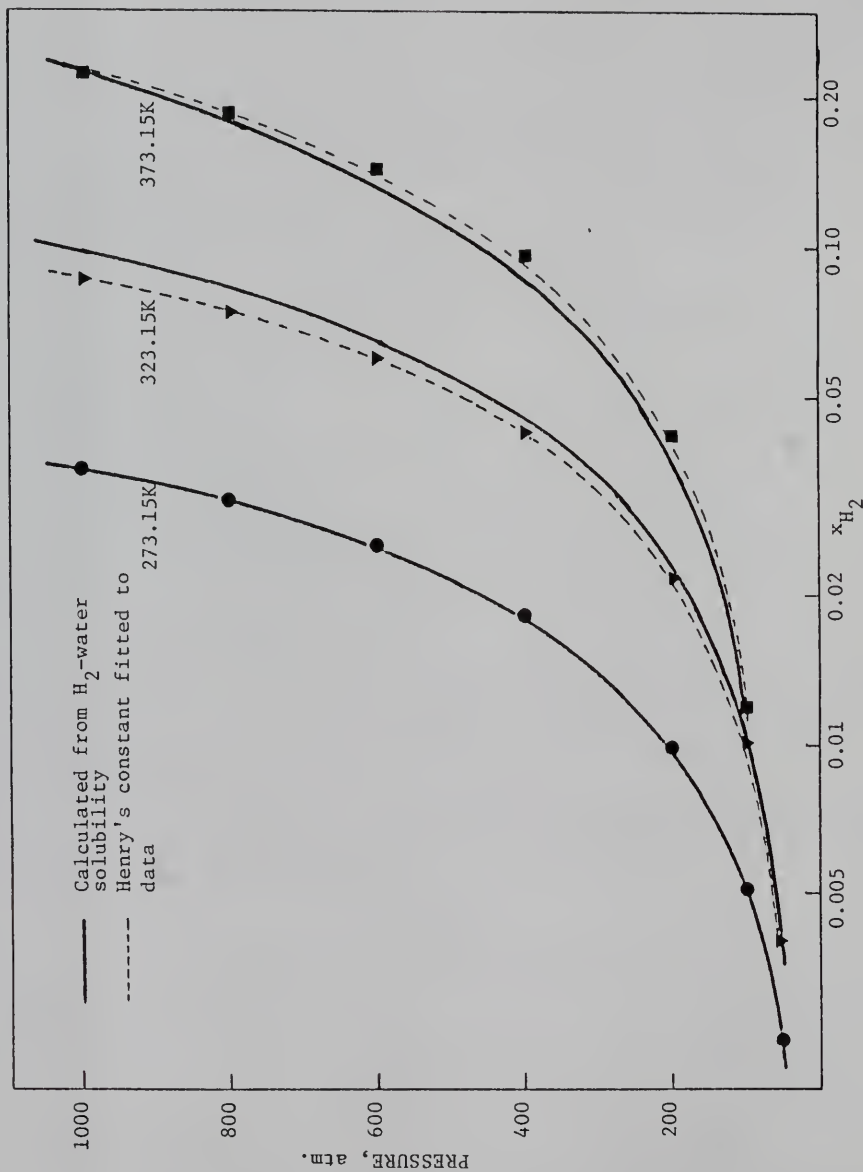
Figure 6-2. Solubility of hydrogen in ammonia calculated from solubility of hydrogen in water. $K_{H_2-H_2O} = -0.24$, $K_{H_2-NH_3} = 0.099$

temperature range considered, yet a temperature independent binary parameter gives a reasonable prediction. For comparison, we also show the calculated hydrogen solubility if the Henry's constant parameters are directly fitted to the experimental data with our theory for the liquid nonideality.

Figure 6-3 shows the prediction of the vapor-liquid equilibrium of methane-n-decane from methane-water. In this case, the ratio of Henry's constants is approximately 500 yet it is predicted to reasonable accuracy. Figure 6-4 shows a plot of the predicted Henry's constants against temperature. We see that there is a large fluctuation in the predicted value. We believe the error is due to sensitivity of the numerical calculations to the solvent molar volume. The molar volumes of water agree with data from many sources and therefore are likely to be correct. However, at the two lowest temperatures we have two sources for the molar volume of saturated n-decane.[1,6] At both temperatures Henry's constant calculated with the data from Snyder and Winnick give a smoother variation of Henry's constant with temperature, but there is still a large fluctuation which is unaccounted for. This problem underscores the sensitivity of the calculation to the liquid density and the necessity for good volumetric data, particularly if the solvents are very dissimilar.

The investigations of this section indicate that, although sensitivity may preclude prediction of the binary parameter, a binary parameter calculated from Henry's constant data at a single temperature will predict the temperature dependence of Henry's constant ratio.
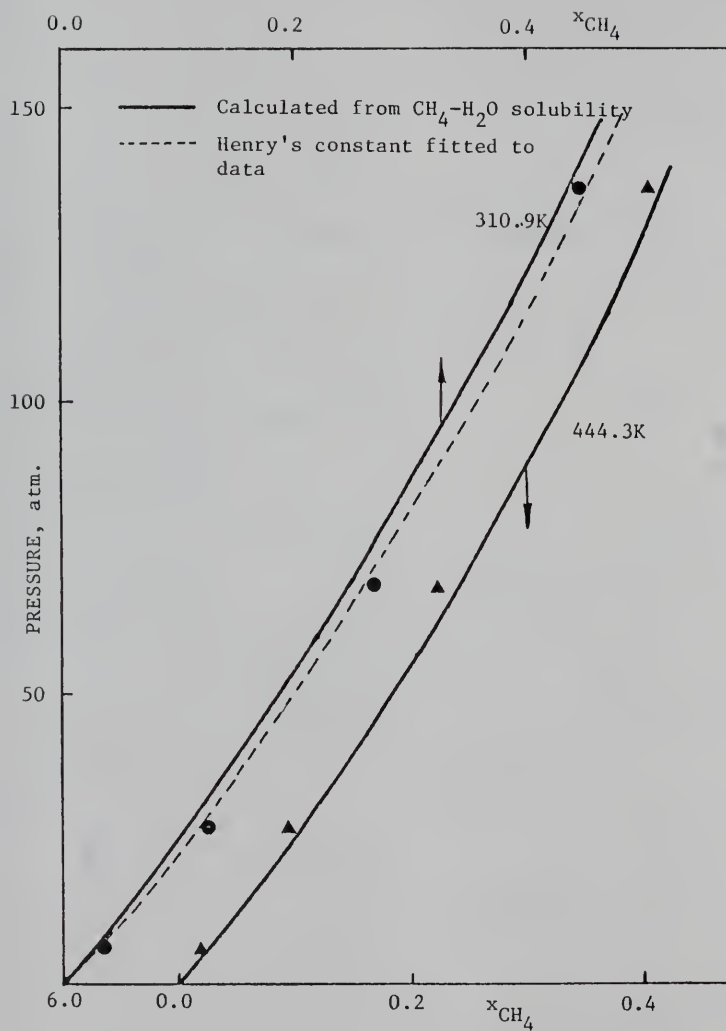
Figure 6-3. Solubility of methane in n-decane calculated from the solubility of methane in water. $K_{CH_4-H_2O} = -0.02$, $C_{CH_4-C_{10}H_{22}} = 0.092$
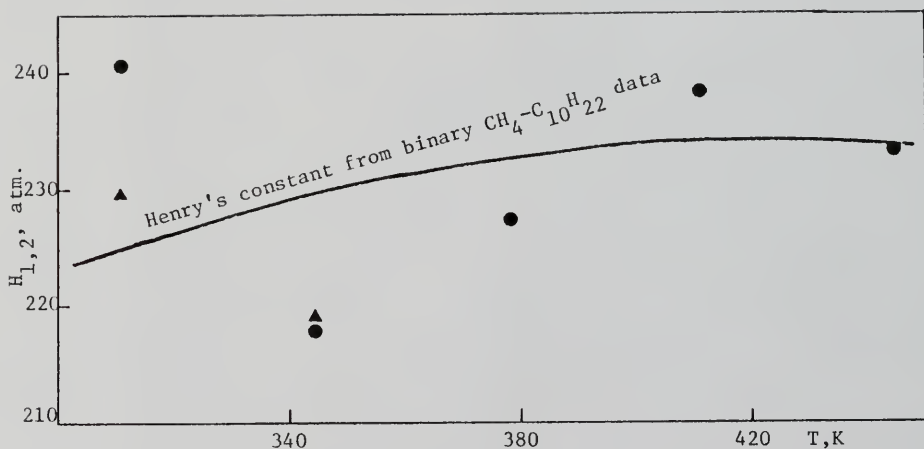
Figure 6-4. Fluctuation of Henry's constant with temperature calculated with volumetric data of Sage et al.[6] (●●●) and Snyder and Winnick[1] (▲▲▲). Henry's constants are calculated from Henry's constant of methane in water

Further, the binary parameters for mutual consistency of Henry's constants will give good predictions of liquid nonidealities.

6.3 Solubility of Hydrogen in Coal Oils

K.C. Chao and coworkers[2-4] have taken data on the solubility of hydrogen in various coal oils. A means of predicting the solubility of hydrogen in these liquids is very important for coal liquefaction and thus we have undertaken to apply our method to the correlation of this set of data.

These systems are no different from those we have already described, but here much of the required input data are lacking. There are no compressibility data for the pure liquids and thus we have no means of estimating the pure component parameters; we do not have available any pure liquid saturated volume data, even the critical constants of some of the liquids have not been experimentally determined.

We have estimated the saturated molar volumes of the liquids by using the Rackett equation[5] since Chao et al. have published values of the critical temperature, critical pressure, the Pitzer acentric factor, and the molar volume at 25°C. One approach we took was to use the methods of Chapter 5 to correlate the data where, in addition to fitting the Henry's constant parameters, we also fit the characteristic parameters of the solvent. This results in an excellent correlation of the data even while assuming a zero value of the binary interaction. But since 5 parameters were fitted this is not surprising.

However, to illustrate the predictive value of our method, we have used the approach of this chapter. For all the systems we have

Table 6-3

Correlation of Hydrogen Solubility in Coal Oils

	T_c^1, K	V_c^1, $\frac{cc}{gmol}$	T^{*2}, K	V^{*2}, $\frac{cc}{gmol}$	K_{12}	Average[3] Error	Temp. range K	Max. Pr, atm.	Max. x_1
Quinoline[4]	794.5	403.	800.	380.0	0.0	0.001	463-702	250	0.207
Tetralin	716.5	438.	693.	454.2	0.0	0.004	463-662	250	0.282
Diphenylmethane	770.2	527.	700.	586.1	0.0	0.007	463-702	250	0.306
Bicyclohexyl	731.4	577.	709.	649.0	0.0	0.007	462-702	250	0.424
1-Methylnaphthalene	772.2	462.	700.	486.6	0.0	0.005	463-702	250	0.295
m-Xylene	617.0	376.	722.	385.0	0.0	0.003	462-582	250	0.324
m-Cresol	705.9	312.	706.	335.5	0.0	0.002	462-662	250	0.235

[1]References 2-4.

[2]From fitting data.

[3]Average error = $\sqrt{\frac{1}{n_d} \sum_{i=1}^{n_d} (x_{1_i}^{exp} - x_{1_i}^{calc})^2}$

[4]For quinoline, $\ln H_{12} = 9.1447 - 1.629 \times 10^{-3}T - 2.552 \times 10^{-6}T^2$
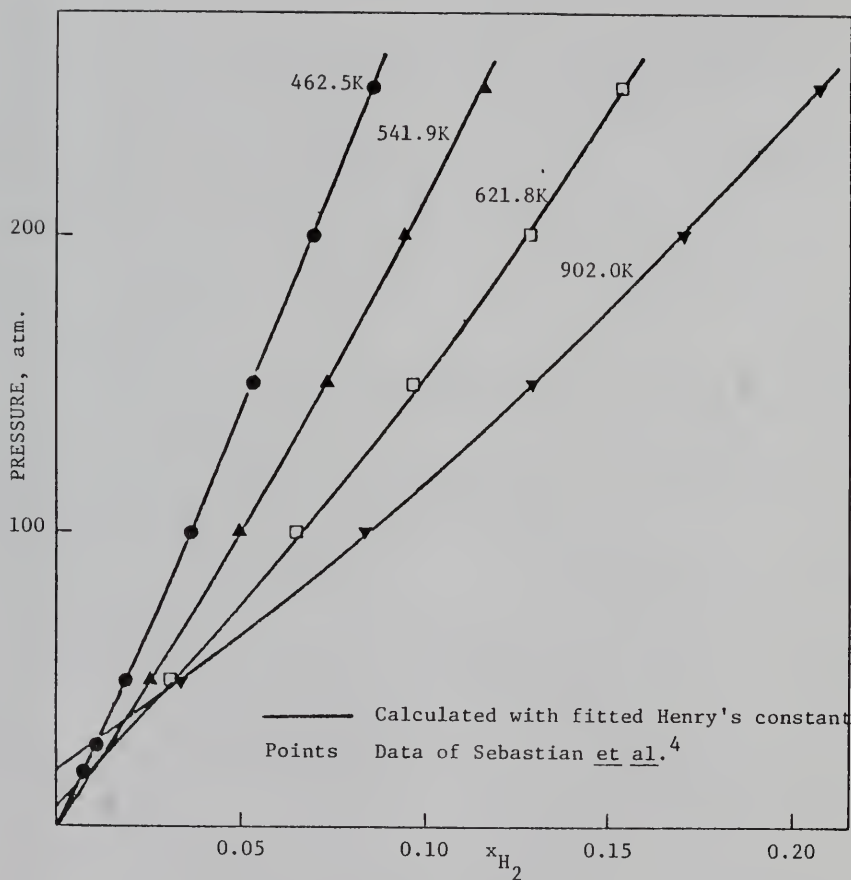
H_{12} - atm

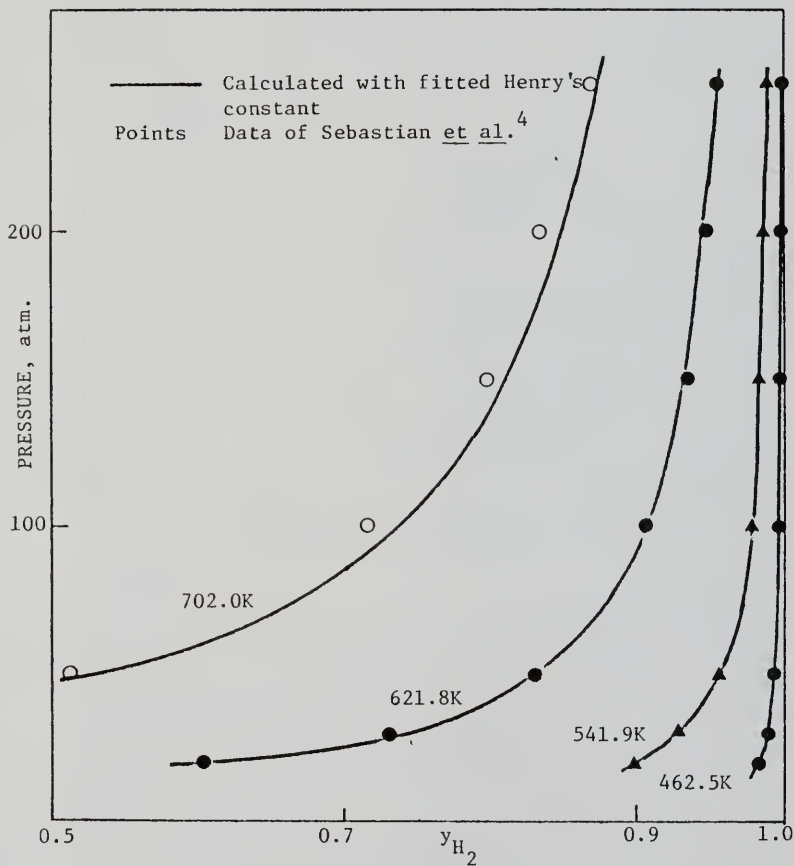T - K

Figure 6-5. Solubility of hydrogen in quinoline

Figure 6-6. Vapor composition of hydrogen-quinoline solutions

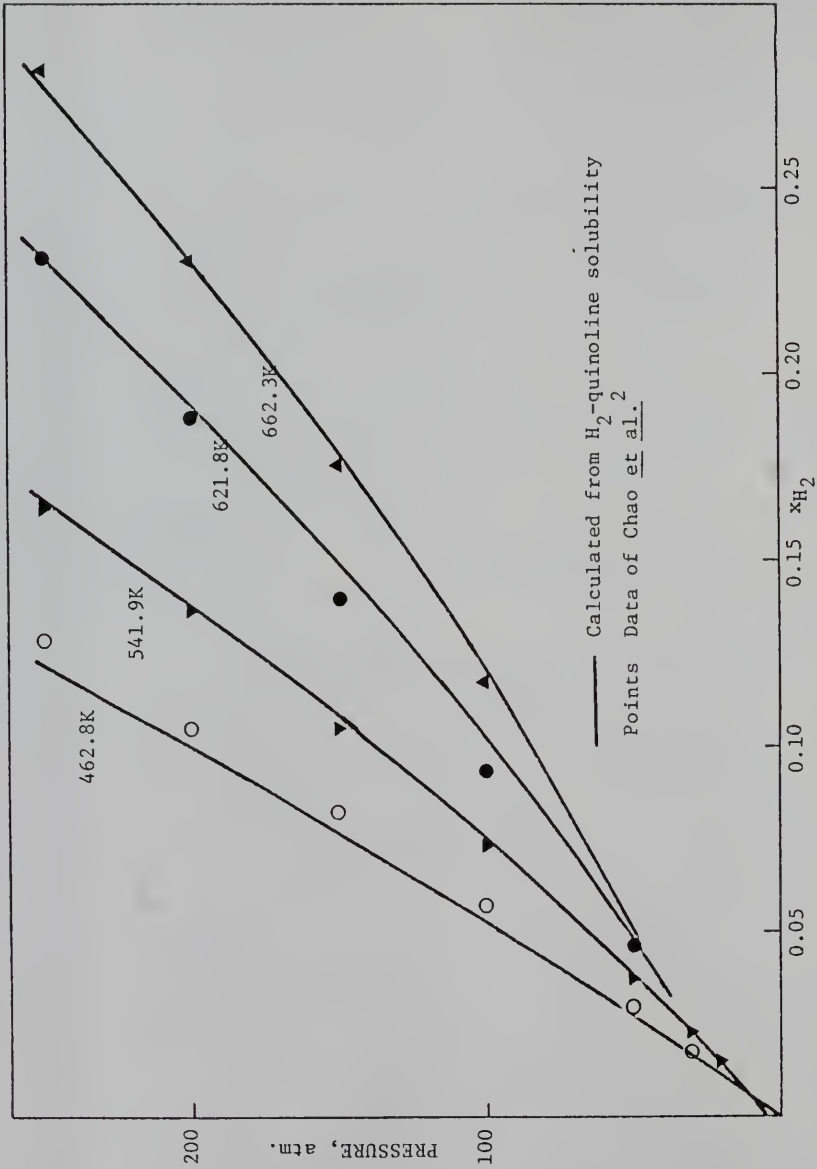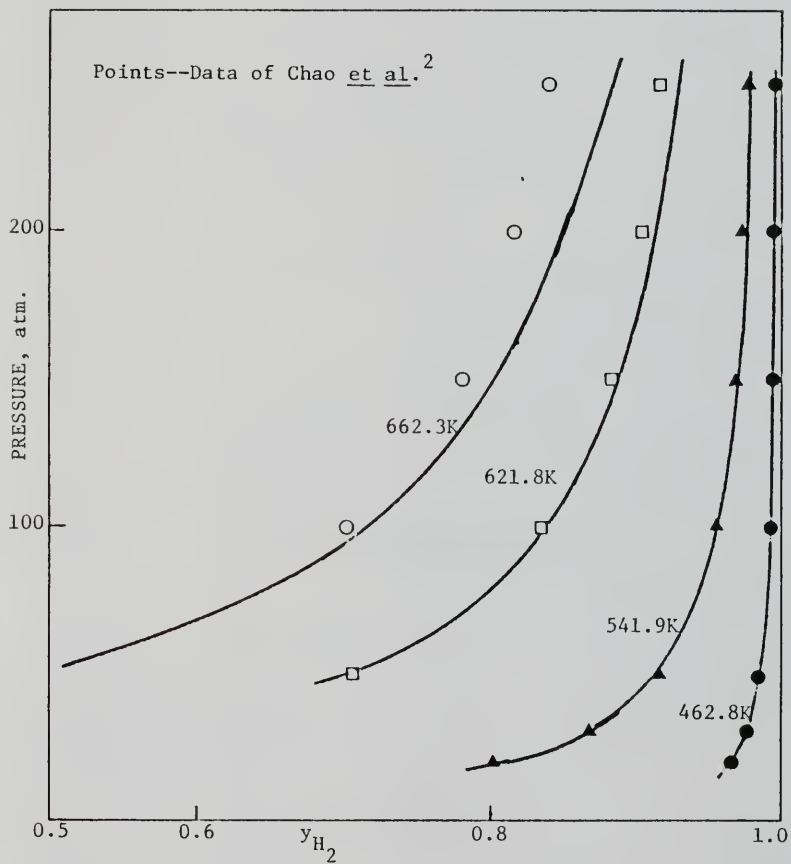Figure 6-7. Solubility of hydrogen in tetralin calculated from the solubility of hydrogen in quinoline

Figure 6-8. Vapor composition of H_2-tetralin solutions calculated from the solubility of hydrogen in quinoline
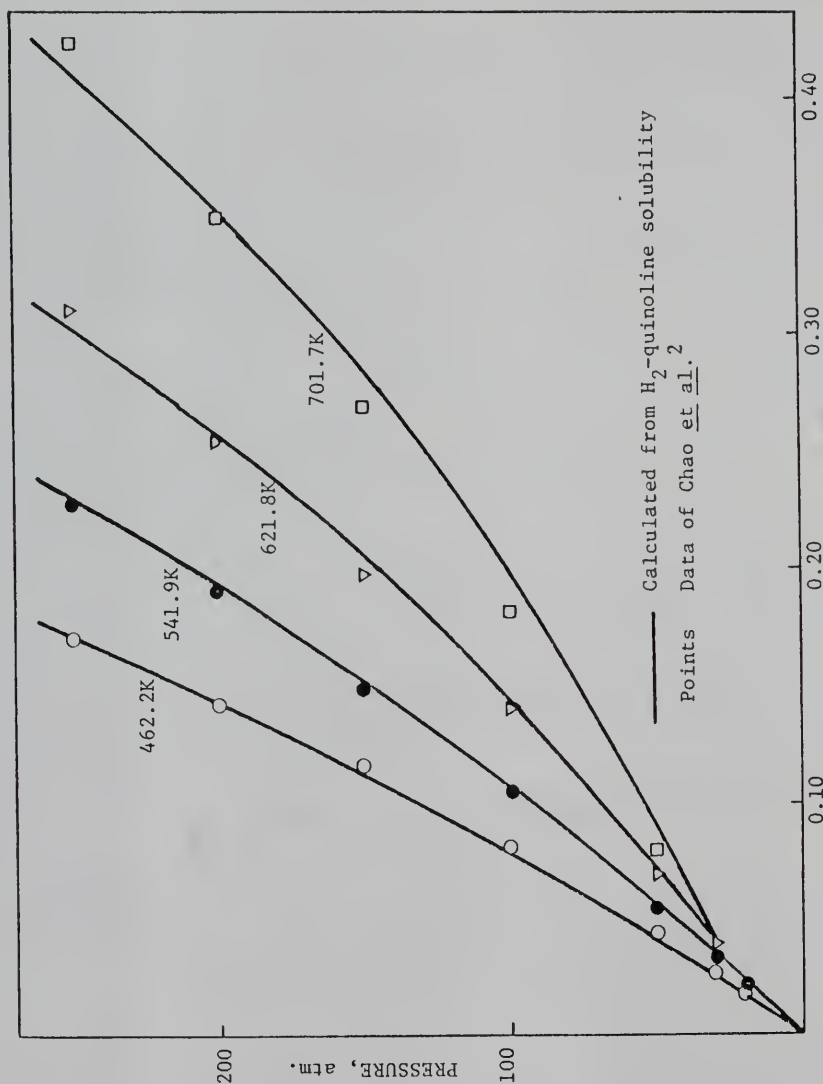
Figure 6-9. Solubility of hydrogen in bicyclohexyl calculated from the solubility of hydrogen in quinoline
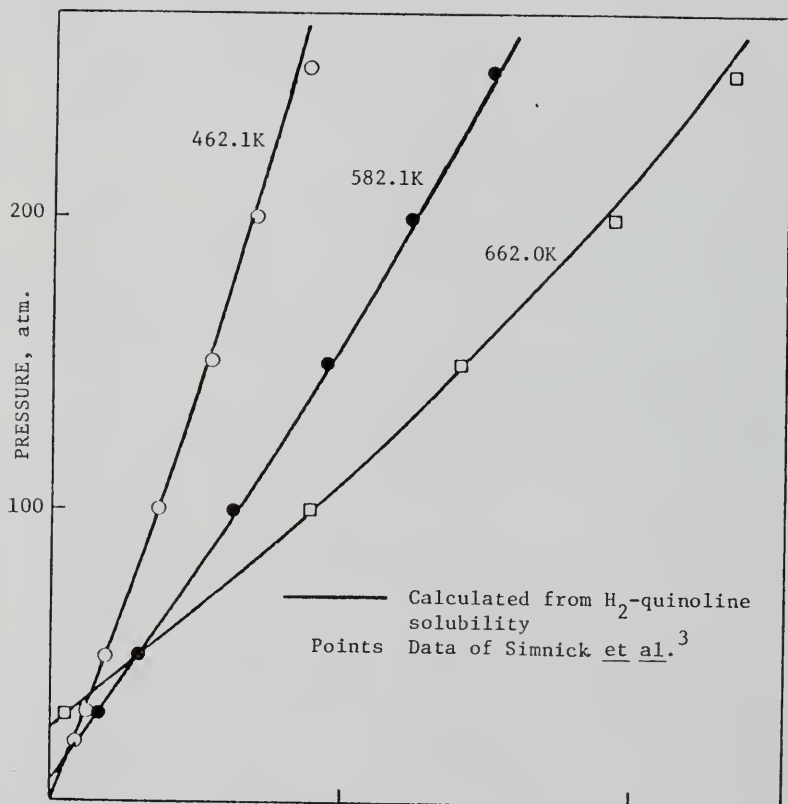
Figure 6-10.   Solubility of hydrogen in m-Cresol calculated
from the solubility of hydrogen in quinoline

assumed a zero value for the binary parameter. We chose quinoline as the reference solvent since it gives the best agreement when fitting Henry's constant parameters to experimental data and also because this system covers the entire temperature range for all coal oil data. For quinoline the characteristic temperature was chosen equal to the critical temperature and the characteristic volume was then obtained by fitting the experimental vapor-liquid equilibrium data. Finally for all the other coal liquids the two characteristic parameters were obtained by fitting the experimental data using hydrogen at infinite dilution in quinoline as the reference state. Comparisons with experimental data are shown in Figures $6-5 - 6-10$. In most cases the agreement with experimental data is quite good; in only very few cases is the deviation in the liquid mole fraction greater than 0.01. For quinoline and tetralin we also show comparisons with the predicted and experimental vapor mole fractions. In all cases the agreement with the experimental composition is quite good except at high temperatures where again the predicted y_1 is slightly high. A summary of the parameters and results for all systems is given in Table 6-3.

On the basis of our experience above we expect quite good agreement if the characteristics were obtained from pure solvent volumetric data and binary parameters were predicted or fitted.

References for Chapter 6

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CHAPTER 7
GENERAL FORMULATION FOR MULTICOMPONENT SYSTEMS

Our theory is formulated to evaluate the change in thermodynamic properties due to any change in the state of the system. Thus, in principle, the arbitrary multicomponent system poses no problem. But there are some kinds of properties which the simple two-parameter theory cannot evaluate to adequate accuracy; and further, as we have shown in the previous chapter, sometimes the parameters of the theory have to be adjusted to ensure mutual consistency of the input data.

We have established all but one aspect required for the general formulation: the prediction of Henry's constants in mixed solvents. Therefore in this chapter we first investigate the ability of the theory to predict Henry's constants in mixed solvent systems and then formulate our suggested approach to an arbitrary multi-component system. The formulation is tested by comparison with experiment for the only system for which extensive data are available, that of n-butane-n-decane-methane.

7.1   Henry's Constant in Mixed Solvents

Prediction of Henry's constants in mixed solvents is a natural outcome of the approach of Chapter 6. Consider the case where the binary parameters have been adjusted to ensure mutual consistency of a solute in several solvents. Now Henry's constant of the solute in any mixed solvent state can be evaluated by Equation (2-25). This requires the

molar volume of the mixed solvent state and therefore excess volume data for the solvent mixture must be available. Since Henry's constants have been made mutually consistent, the calculation will yield precisely the same result regardless of which solvent is chosen as the reference.

Figures 7-1 and 7-2 show comparison with the experimental data for the system carbon dioxide-methanol-benzene[1] and carbon dioxide-methanol-water[1] respectively. The solvent-solvent excess volumes have been obtained from experimental data.[2] The binary interaction parameters have been chosen by assuming a value of -0.20 for carbon dioxide-water since this was the optimum value we obtained when fitting binary data. The results for this system are insensitive to the value chosen for the "reference" binary parameter. Thus for instance in Figure 7-2 the results would be hardly changed if the binary parameter for carbon dioxide-water were 0.0. However, the results are quite sensitive to the excess volume. In Figure 7-2 we show the prediction of mixed solvent Henry's constants if a small negative excess volume is assumed rather than the actual values.

Figure 7-3 shows similar results for the system carbon monoxide-nitrobenzene-benzene.[3] In this case the carbon monoxide-benzene binary parameter has been assumed to be 0.10; this value gives the best fit of binary nonideality. Again, the results are insensitive to the value assumed.

Finally, in Figure 7-4 we show results for the argon-methanol-water system.[4] Here we show a prediction of mixed solvent Henry's constants for two values of the argon-water binary parameter. In

Figure 7-1. Calculation of Henry's constant of carbon dioxide (1) in the mixed solvent methanol (2)-benzene (3), T = 293K; $K_{1,2} = -0.20$; $K_{1,3} = -0.235$

Figure 7-2. Calculation of Henry's constant of carbon dioxide (1) in the mixed solvent methanol (2)-water (3), T = 293K; $K_{1,2} = -0.20$; $K_{1,3} = -0.210$
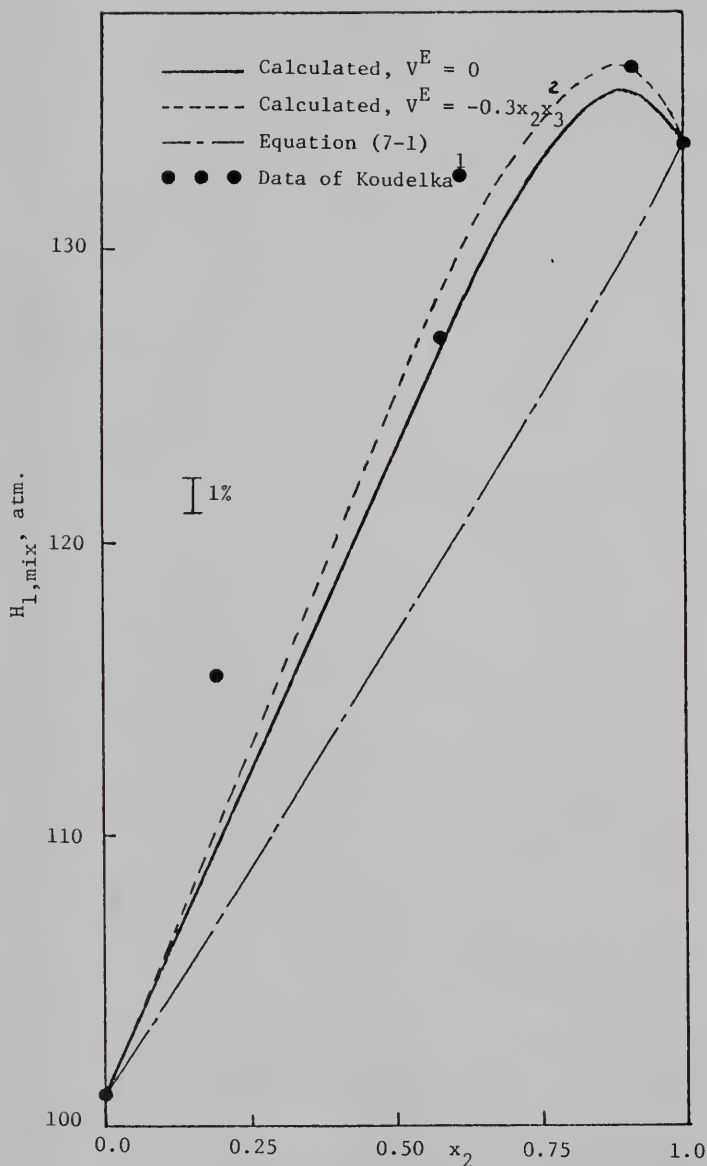
Figure 7-3. Calculation of Henry's constant of carbon monoxide (1) in the mixed solvent nitrobenzene (2)-benzene (3), T = 298K; $K_{1,2}$ = -0.039; $K_{1,3}$ = 0.10
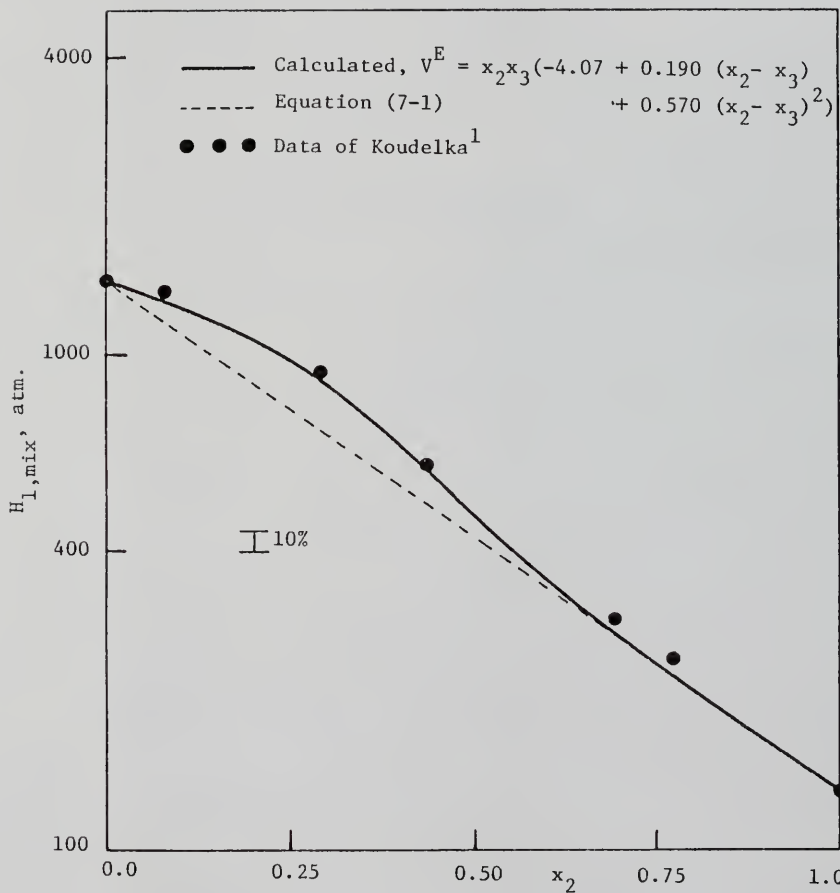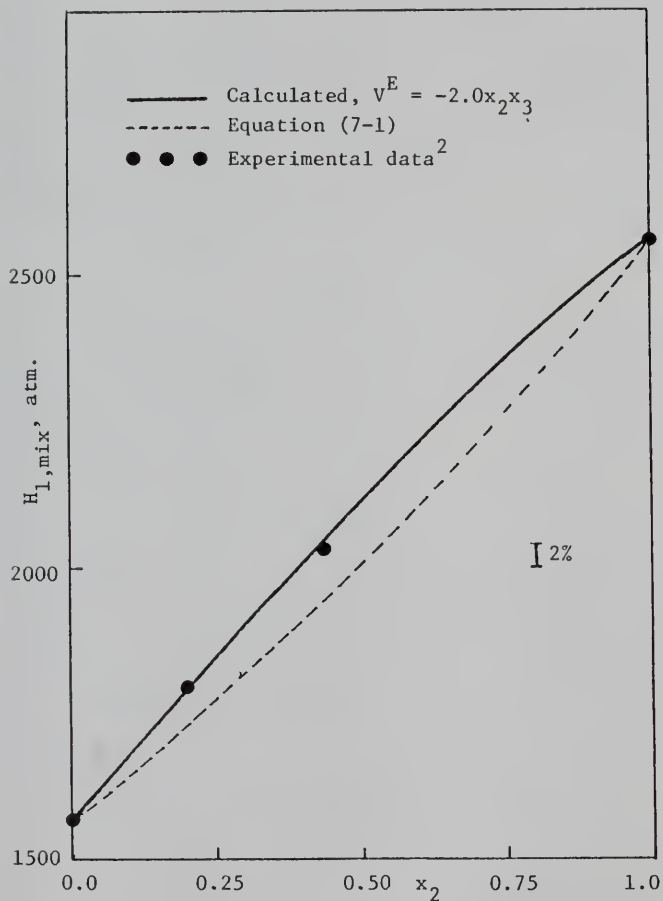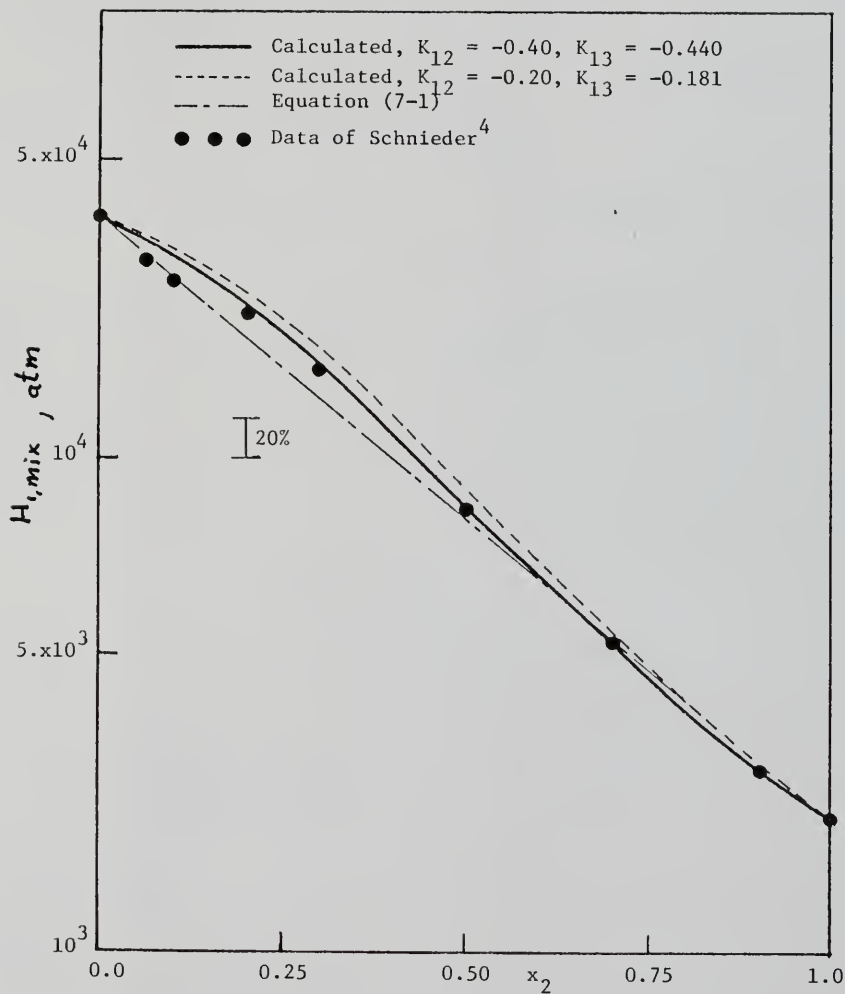
Figure 7-4. Calculation of Henry's constant of argon (1) in the mixed solvent methanol (2)-water (3), $T = 288K$; $V^E = x_2 x_3 (-4.07 + 0.19(x_2-x_3) + 0.57 (x_2-x_3)^2)$

this case the results are sensitive to the binary parameter and the unlikely value of -0.40 is required to give a fair prediction for most of the composition variation. While the inability of the theory to describe the variation with composition in the water region could be attributed to the break-up of the complex water structure which the theory does not describe, since the data for CO_2 in these solvents is well correlated, we cannot really be sure what the inadequacy is. In addition, the sensitivity of this system to the binary interaction parameter, as opposed to the behavior of other systems, also leaves the correlation with some uncertainty.

We will have to investigate many more systems before a more definite statement can be made, but it is likely that the theory will provide a reasonably accurate description of Henry's constants in mixed solvents if the systems are nonaqueous. In any case, the prediction is better than the zeroth-order approximation,[5]

$$\ln H_{1m} = x_2 \ln H_{12} + x_3 \ln H_{13} \tag{7-1}$$

though perhaps not as accurate as some of the recent empirical rules.[14] However, even if Henry's constant of a solute in a mixed solvent has to be predicted from a theory which is different from the present formulation, the methods of the next section can be used to describe the nonideality.

7.2 Discussion and Formulation of an Arbitrary System

Consider an arbitrary n-component system containing n_s solvents and the rest solutes, where components $1, 2, \ldots, n_s$ are solvents. We

repeat that a solute is a supercritical component or at least one
whose most convenient reference state is infinite dilution; and a
solvent is a subcritical component whose most convenient reference
is the pure state. Now we want to formulate the approach to solving
any vapor-liquid equilibrium problem. As before we assume that vapor-
phase fugacities can be calculated by already existing methods and
confine ourselves to the calculation of liquid-phase properties.
Hence the problem reduces to calculating the liquid fugacities at
any temperature T, pressure P^f, and liquid composition $(x_1^f, x_2^f, \ldots, x_n^f)$.
Of course, it is the value of T which determines whether a substance
is a solute or a solvent, and if the temperature is decreased a "solute"
could become a "solvent".

We assume that the pure component parameters have been deter-
mined for all the components and approximate estimates are available
for all the binary interaction parameters, say, by the methods of
Chapters 5 and 6. We also assume that we have available as input
data the saturated molar volumes and pressures for all the solvents
of the system and the matrix of Henry's constants of the $n-n_s$ solutes
in the n_s solvents. (If some of Henry's constants are not available
they can be predicted to reasonable accuracy by the methods of Chapter 6,
but here for simplicity we assume that all Henry's constants are avail-
able.) Finally, we also assume that the mixed solvent excess volume
data is available.

The calculation is most conveniently broken down into three
steps shown schematically in Figure 7-5:

Initial Pure Component
Saturated State
for Solvents $1,\ldots,n_s$

$X_i^o = 1$

$P = P_i^{sat}(T)$

$v = v_i^{sat}(T)$

Mixing of Solvents →

Intermediate Mixed
Solvent State

$X_i^{MS} = \dfrac{X_i}{\displaystyle\sum_{j=1}^{MS} X_j}$ $i=1,\ldots,n_s$

$P = P^{MS}(T,\underline{X})$

$v = v^{MS}(T,\underline{X})$

Determine $(f_i/X_i)^{MS}$ for all
species (Steps 1,2)

Addition
of
Solute →

Final State

$X_i = X_i^f$

$P = P^f$

$v = v^f$

Determine

$\gamma_i = (f_i/X_i^f)/(f_i/X_i)^{MS}$

for all species (Step 3)
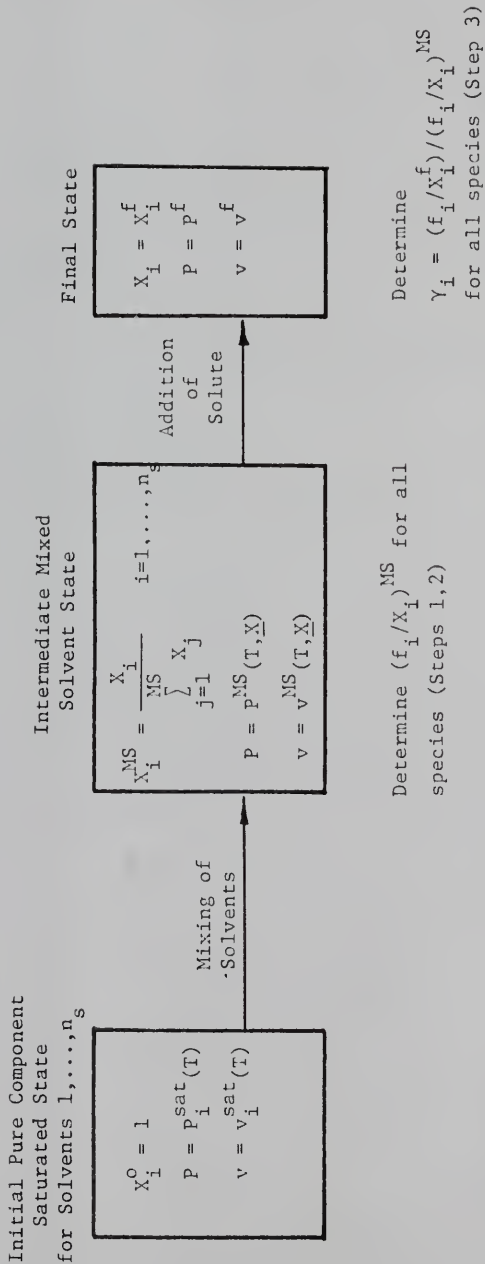
Figure 7-5. Schematic diagram of approach to multicomponent case at constant temperature

1. Calculation of $(f_i/x_i)^{MS}$ of the solvent components in the mixed solvent (solute-free) reference. The mixed solvent reference state is one where all the solute components are present only at infinite dilution. Thus,

$$x_i^{MS} = \frac{x_i}{\sum_{j=1}^{n_s} x_j} \quad , \qquad i=1,\ldots,n_s$$

$$x_i^{MS} = 0 \quad , \qquad i=n_s+1,\ldots,n \qquad (7-2)$$

This calculation requires the solution of the solute free vapor-liquid equilibrium $(\underline{y}^{MS}, p^{MS})$.

2. Calculation of $(f_i/x_i)^{MS}$ of the solute components in the mixed solvent reference state.

3. Calculation of the activity coefficients γ_i and volume v^f of all components due to a change in the state of the system from an initial state of $\underline{x}^{MS}, p^{MS}, v^{MS}$ to a final state of $\underline{x}^f, p^f$.

Our method cannot quantitatively describe step 1. The numerical values are quite sensitive to the details of the intermolecular potential which the theory ignores. Further, the activity coefficient derivative contains small differences of large numbers. However, the calculation can be performed accurately by any of several existing methods.[6]

The calculation of the quantities in step 2 have been discussed above and for most systems we expect satisfactory results.

Our theory is best suited for the calculation of the quantities involved in step 3 since this change corresponds to the same one we performed for the binary gas-solvent case. Here the mixed solvent

corresponds to the saturated pure solvent and final multicomponent state corresponds to the binary system at an elevated pressure with a finite solute composition. Thus all the arguments we made for the advantage of our approach for the binary system are valid here and we expect the same degree of success as we have had for the binary case for all systems including those containing polar components.

The numerical calculations involved are no more complex than in the binary case and in the computer program the same subroutine is used for all systems (see description of subroutine ACTCF in Appendix C). However, the binary interaction parameters must be specified for all interactions including those between solvents. The solute-solvent binary parameter may have to be evaluated from binary gas-solvent data, but the indications are that the calculation of step 3 is virtually insensitive to the value of ~~these~~ *solvent-solvent* parameters and even zero values will yield good results.

The use of our approach for step 3 is also advantageous because it provides a complete description of the changes from the mixed solvent reference state to the final state. Thus the activity coefficients are independent of the variation of the mixed solvent Henry's constants unlike the Chueh-Prausnitz formulation.[8,12]

In summary, our formulation for the arbitrary multicomponent case is as follows: We use the mixed solvent as an intermediate reference state. For this state the fugacities of the solute-free system are evaluated by some other correlation while in most cases our theory can be used to evaluate the solute fugacities. Finally, our theory is then used to evaluate the change in fugacity of all

components due to a change from the intermediate reference state $\underline{x}^{MS}$, P^{MS}, v^{MS} to the final state $\underline{x}^f, P^f$.

7.3 Application to the System: n-Butane-n-Decane-Methane

The n-butane-n-decane-methane ternary system provides a reasonable test of our multicomponent formulation since it contains two solvents. Therefore, we decided to compare the prediction of our formulation with the experimental data of Sage and Lacey.[7] We have done a bubble pressure calculation, i.e., calculation of the saturation pressure and vapor composition from the temperature and the liquid composition.

We used the modified Redlich-Kwong equation[8] for the description of the vapor phase. The Wilson equation was used to calculate the fugacities of the solvents. Henry's constants of methane in the pure solvents were obtained from the binary data (see Chapter 5).

The method we adopted to evaluate liquid fugacities is the same as the one described above. The binary parameter of methane-n-butane was fixed at 0.04 and the methane-n-decane binary parameter was evaluated to maintain consistency of Henry's constants. The value of 0.086 obtained is consistent with the value obtained by fitting high-pressure methane-n-decane data. Now we used the experimental volumetric data of Reamer et al.[9] to evaluate the mixed solvent Henry's constants. The points in the upper part of Figure 7-6 show the experimental data and the dashed line shows our representation of it. With this excess volume representation the bubble pressures were high for systems containing mostly n-decane and low for systems containing mostly n-butane.

We investigated whether this discrepancy could be due to experimental error in the excess volume of Reamer et al.[9] All other experimental excess volume of hydrocarbon mixtures,[10] supported by the Brønsted congruence principle,[11] indicates that the excess volume is skewed towards high mole fractions of the smaller component and that a simple expression symmetric in volume fraction is sufficient to correlate it. Therefore, we have used such an expression with the same maximum excess volume as indicated by Reamer et al. (full line in the upper part of Figure 7-6).

The lower part of Figure 7-6 shows the calculated mixed solvent Henry's constant corresponding to Reamer's data and our postulated excess volume respectively. Table 7-1 shows the calculated bubble pressures and vapor compositions and comparison with the data of Sage et al.[7] when our postulated excess volume is used. The results are as good obtained for the binary systems (Chapter 5), but they should be viewed with caution since they are obtained with a plausible but experimentally unconfirmed excess volume function. We again note the high sensitivity of the calculation to the input volumetric data and the importance of its reliability for practical application of the method.

7.4 Application to Gas Solubility in Complex, Uncharacterized Solvent Mixtures

One final question remains: Can the theory be used to predict gas solubility in complex liquid mixtures? We propose the following method based on our experience with the theory. Consider the solubility of a gas in a liquid mixture where no component has a high vapor pressure
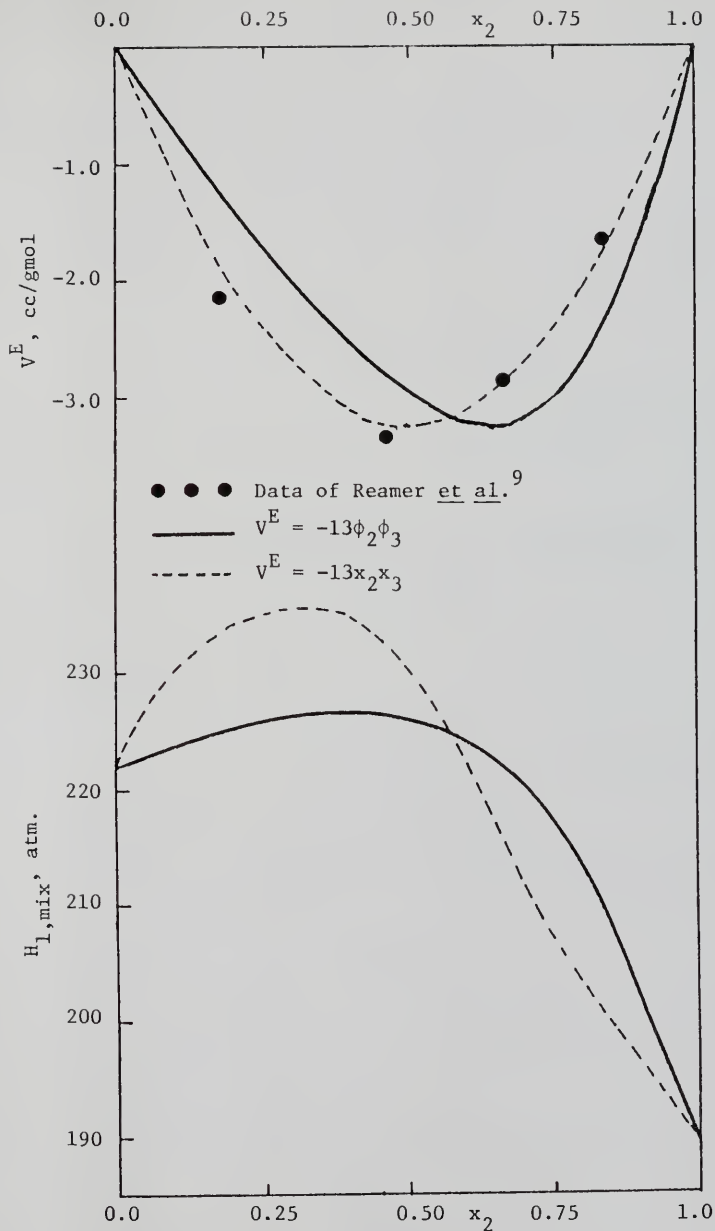
Figure 7-6. Excess volume of n-butane (2)-n-decane (3)
and calculated Henry's constant of
methane in above mixed solvent. T = 344.3K;
K_{12} = 0.040; $K_{1,3}$ = 0.086

Table 7-1

Comparison of Predicted and Experimental Results for the
System n-Butane-n-Decane-Methane, T = 344.3K

			Experimental					Calculated				
x_1	x_2	x_3	P,atm.	y_1	y_2	y_3	P,atm.	y_1	y_2	y_3		
0.0	0.886	0.114	27.22	0.0	.002	.998	27.673	0.0	0.002	0.998		
0.358	0.538	0.104		.105	.002	.893	29.162	0.135	0.001	0.864		
0.724	0.181	0.095		.267	.001	.737	28.846	0.280	0.001	0.719		
0.911	0.0	0.089		.377	.0	.623	27.005	0.381	0.0	0.619		
0.0	0.792	0.208	54.46	0.	.002	.998	54.492	0.0	0.001	0.999		
0.321	0.481	0.198		.080	.002	.918	56.030	0.086	0.001	0.913		
0.642	0.160	0.198		.184	.001	.816	55.529	0.183	0.001	0.816		
0.788	0.0	0.212		.254	0	.746	54.641	0.249	0.0	0.751		
0.0	0.750	0.250	68.07	0.	.002	.998	67.831	0.0	0.001	0.999		
0.152	0.606	0.242		.036	.002	.963	67.734	0.038	0.001	0.961		
0.305	0.457	0.238		.075	.002	.923	68.503	0.077	0.001	0.922		
0.602	0.151	0.247		.172	.002	.829	69.024	0.165	0.001	0.835		
0.728	0.0	0.271		.242	0	.757	68.393	0.228	0.0	0.772		
0.0	0.702	0.298	85.09	0.0	.002	.998	84.173	0.0	0.001	0.999		
0.283	0.425	0.291		.071	.003	.927	86.071	0.069	0.001	0.930		
0.423	0.282	0.296		.111	.003	.886	87.304	0.107	0.001	0.891		
0.652	0.0	0.348		.241	0	.754	86.170	0.217	0.0	0.783		
0.0	0.657	0.343	102.11	0	.003	.997	100.587	0.0	0.001	0.999		
0.264	0.397	0.339		.046	.003	.930	102.651	0.064	0.001	0.934		
0.392	0.261	0.347		.108	.003	.889	104.089	0.101	0.001	0.898		
0.567	0.0	0.433		.256	0	.744	104.730	0.212	0.0	0.788		
0.0	0.577	0.423	136.10	0.	.004	.996	132.067	0.0	0.002	0.998		
0.229	0.343	0.428		.062	.005	.933	134.712	0.058	0.002	0.941		
0.412	0.103	0.485		.167	.006	.826	133.196	0.126	0.001	0.872		
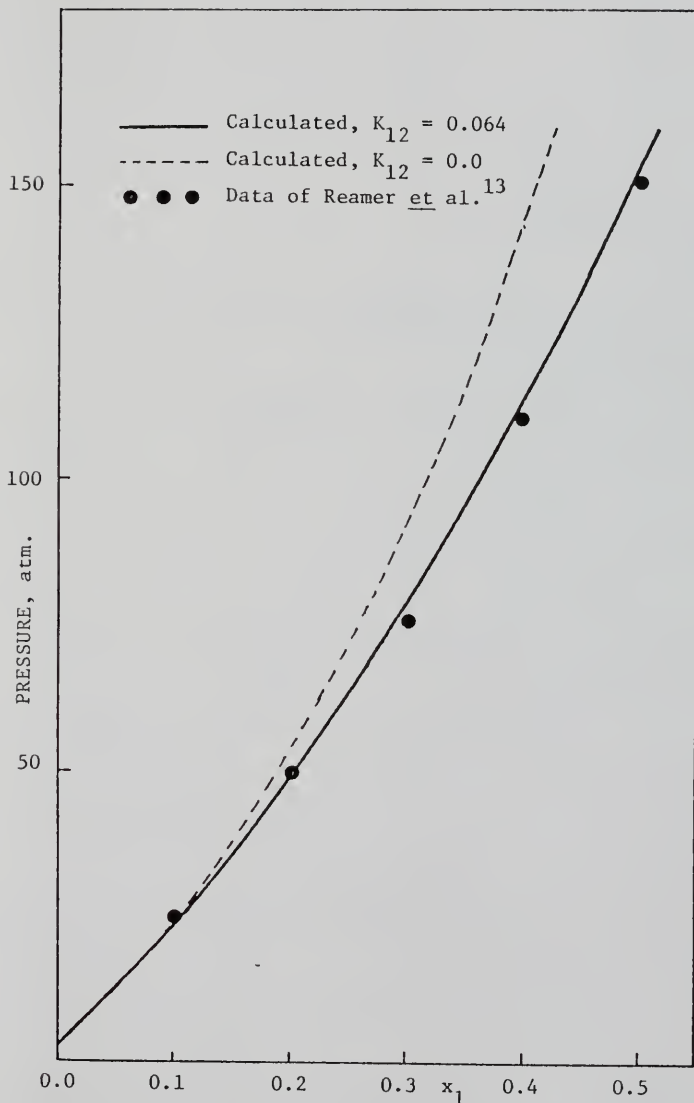
Figure 7-7. Calculated bubble pressure of methane (1)-
n-butane-n-decane $(x_{C_4}/(x_{C_4} + x_{C_{10}}) = 0.4631)$
with butane-decane mixture treated as a pseudo
component (2). T = 310.93 K

(say < 1 atm). In this case at high pressures we can assume that the vapor phase contains very little of the solvent components. Thus we can calculate the gas solubility by

$$x_g \approx \frac{P\phi}{H_g\gamma_g} \tag{7-3}$$

ϕ_g can be calculated from any equation of state valid for the gas; H_g can be calculated from a low-pressure solubility measurement; and γ_g can be calculated from our theory by treating the solvent mixture as a pseudo component where the parameters are obtained by compressibility measurements and the binary parameter is assumed equal to zero.

This method is likely to be useful for hydrogen solubility in solvent mixtures since the calculated nonideality is insensitive to the binary parameter. Unfortunately, we do not have any such data available. Therefore, we tested the method on methane solubility in an n-butane-n-decane mixture at 100°F.[13]

This system requires minor modifications to the above approach. The mixed solvent pressure is not negligible and therefore we modified Equation (7-3).

$$x_g \approx \frac{(P-P^{MS})\phi_g}{H_g\gamma_g} \tag{7-4}$$

Further, the results are sensitive to the binary parameter and it must be estimated. Finally, the pseudo solvent parameters must be estimated. For all these quantities we assumed a simple mixed solvent

mole fraction average. The methane vapor phase was described by the Redlich-Kwong equation.[8] The results are shown in Figure 7-7. (In Figure 7-7 we also show the results if a zero value of the binary parameter is assumed.) The good comparison with experimental data indicates that it is viable to treat the solvent mixture as a pseudo component.

References for Chapter 7

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CHAPTER 8
CONCLUSIONS

In this work we have formulated a practical problem in terms
of fundamental quantities, but have not hesitated to use empiricism
to make the numerical calculations tractable. The result is a simple
method to describe complicated systems. We have investigated all the
various aspects separately and have then formulated the approach to
the general problem. We have only one system where we compare our
general predictions with experimental data and even for it the input
volumetric data appears unreliable. However, we are reasonably
confident that further testing will prove the formulation can provide
an adequate description of multicomponent systems.

Reviewing now our methods, Chapter 1 is an introduction to the
prediction of high-pressure vapor-liquid equilibrium. This chapter
shows why it is advantageous to describe liquid fugacities in terms
of a reference state and to describe all deviations from this reference
state by a single model.

Chapter 2 describes our solution theory and shows how it can
be used to provide expressions for the nonideality of multicomponent
mixtures in terms of pair direct correlation function integrals
(hereafter referred to as DCFI). These expressions are simple to
implement and thus if the DCFI can be evaluated at any condition
the numerical calculations pose no problem whatsoever.

It has been found that for dense fluids the DCFI are insensitive to the details of the intermolecular interactions. Thus we have proposed a simple empirical model based on research findings of fluid structure which ensures that the numerical calculations are tractable and rapid. The model contains only two parameters for each component and a binary parameter for each pair of components.

Chapter 4 describes the application of the method to the compressibility of pure fluids. This is useful in itself, but more important it provides a means of determining the solvent parameters.

Chapters 5-7 describe the application of the model to the prediction of fugacities in liquid mixtures containing supercritical components. Our objective has been to use the model to evaluate liquid fugacities at any arbitrary condition by using only few easily accessible input data. For binary gas-solvent systems the only input data required is the molar volume, vapor pressure and fugacities of both components at the reference state (pure, saturated solvent). The results of Chapter 5 indicate that our model provides a very good description of binary nonideality. This gives us confidence that in the arbitrary multicomponent case the model will accurately predict the activity coefficients for a change from any solute-free reference system to any system in which solutes are present.

We have also investigated the evaluation of fugacities in the mixed solvent state from easily measurable pure solvent quantities. The evaluation of mixture solvent fugacities from pure component properties cannot be evaluated by our model to sufficient accuracy,

but existing methods can perform this calculation. Chapter 6 describes a preliminary investigation of the solute fugacities in the mixed solvent system; here we perform the calculation of Henry's constant of a solute in one solvent from Henry's constant of the same solute in another solvent. Then in the beginning of Chapter 7 we investigate the prediction of Henry's constants in mixed solvents. The results are good except for some aqueous systems.

The multicomponent formulation follows easily from the above results. We require all the pure component parameters and for each solute the binary parameter in any one (reference) solvent. Now at each temperature the input data required is the molar volumes and pressures of all the solvents in the saturated state, the matrix of Henry's constants of the solute in the solvents (some of which may be determined using the methods of Chapter 6), and the excess volume of the solvent mixture. The solute-solvent binary parameters are first evaluated by ensuring mutual consistency of Henry's constants in the pure solvents, and then Henry's constants in the mixed solvent state can be evaluated using excess volume of mixing data. The solvent fugacities in the mixed solvent state must be evaluated by some method such as with Wilson's equation or UNIQUAC; this calculation also yields the mixed solvent bubble pressure. Finally, our model is used to evaluate fugacities at any condition where solutes are present using the mixed solvent as the (unique) reference state. Chapter 7 has a detailed description of the formulation and the application to the system n-butane-n-decane-methane system.

APPENDIX A

MICROSCOPIC MODEL FOR DIRECT CORRELATION FUNCTION INTEGRALS

We have also investigated a microscopic model for the direct correlation function integrals. It is in the same spirit as the one described in Chapter 3: the choice of the model is consistent with the three considerations we have enumerated (see the beginning of Chapter 3).

A.1 Pure Fluid Model

We start with the Percus-Yevick equation[1,2] which relates the correlation functions, g and c, via the pair potential, ϕ

$$g(r)[e^{\beta\phi(r)} - 1] = - c(r) \tag{A-1}$$

The approximation has been shown to be a good one especially for hard sphere fluids.[1]

A quantity $y(r)$ can be defined as

$$y(r) = g(r) \, e^{\beta\phi(r)} \tag{A-2}$$

It has been used in perturbation expansions with hard sphere fluids as the reference fluid since at high densities,

$$y^{rf}(r) \approx y^{hs}(r) \tag{A-3}$$

Equation (A-3) can be combined with the Percus-Yevick equation to provide an approximation for the direct correlation function and hence for the direct correlation function integral

$$C = \rho \int y^{hs}(r) \ [e^{-\beta\phi(r)} - 1]d\underline{r} \qquad (A-4)$$

Equation (A-4) is equivalent to Equation (3-3) in the sense that both equations provide expressions for the direct correlation function integral as a function of temperature and density. An interesting consequence of Equation (A-4) is that it predicts the exact second virial coefficient, for in the limit of low densities

$$\lim_{\rho\to0} y^{hs}(r) = 1 \qquad (A-5)$$

$$\therefore \quad \lim_{\rho\to0} \left| \frac{\overline{1}/\rho K_T RT - \overline{1}}{\rho} \right| = - \int [e^{-\beta\phi(r)} - 1]d\underline{r} \qquad (A-6a)$$

$$= 2B_2 \qquad (A-6b)$$

Equation (A-6b) arises in the statistical mechanical virial expansion.[1] (Also, see Equation (3-2).)

We obtain $y^{hs}(r)$ from the solution of the Percus-Yevick equation for hard spheres.[3,4] This has been shown to be very much in error for $r < \sigma$.[5] However, it turns out that it is much better than the exact value of $y^{hs}(r)$ in Equation (A-1) to predict $c^{hs}(r)$. The reason for the apparent anomaly is a fortunate cancellation of errors.

The function $y^{hs}(r)$ also depends on the hard sphere diameter σ which is some unknown function of the pair potential and the state of the fluid. The results are extremely sensitive to σ so a predictive method is unlikely to be successful and we developed an empirical relation. Assuming two-parameter corresponding states theory is valid for this property, σ reduced by the size parameter of the potential must be a universal function of the temperature reduced by the energy parameter of the potential and the density reduced by the size parameter of the potential cubed. We assumed the pair potential was of the form given by Maitland and Smith[6] and then deduced an empirical correlation in a manner entirely analogous to the method described in Chapter 3.

The parameters of the correlation are the size and energy parameters of the pair potential; but for convenience we scaled them to provide parameters which are equal to the critical temperature and volume for the reference substance (see Table A-1). As in Chapter 3 we chose argon (and krypton and xenon suitably reduced[7]) as the reference fluid since a large amount of reliable data is available for these substances (see references 12-17 of Chapter 3). Now the compression data was used to deduce and fit a correlation for the hard sphere diameter. The equations and constants are shown in Table A-1. The representation is quite good except in the critical region. Here, there are some fluid conditions (for example $\tilde{T} = 1.115$, $\tilde{\rho} = 0.6$) where no value of the hard sphere diameter will give a positive compressibility. These regions possibly correspond to the fluid conditions for which the Percus-Yevick equation with our pair potential diverges.

Table A-1

Correlation for Reduced Hard Sphere Diameter

$$KT^*/\epsilon = 1.058 \tag{A-7}$$

$$N_{av}R_m^3/V^* = 0.4209 \tag{A-8}$$

where ϵ, R_m are the energy and size parameters of the Maitland-Smith potential.[6] The constants in Equations (A-7) and (A-8) were calculated by assuming for Argon $T^* = T_c$, $V^* = V_c$ and the pair potential parameters given by Maitland and Smith.

$$\sigma/R_m = \frac{a_1}{a_2 + \tilde{T}} + a_3 \exp -(a_4\tilde{\rho} + a_5\tilde{T}) \tag{A-9}$$

$$a_1 = 0.90327658$$
$$a_2 = 0.019053766$$
$$a_3 = 1.9153663$$
$$a_4 = 0.77038805$$
$$a_5 = 2.54478440$$

$$\tilde{\rho} = \rho V^*$$
$$\tilde{T} = T/T^*$$

As we have done in Chapter 4, this model can be used to predict the compressibility of any liquid if the correct characteristic parameters are chosen. Alternately, liquid compression data of any fluid can be used to fit the characteristic parameters, providing a possible means of parameter determination. The results of the fitting of a few fluids are shown in Table A-2.

A.2 Extension to Mixtures

Equation (A-4) is applicable to all pairs in a mixture.

$$c_{ij} = \rho \int y_{ij}^{hs}(r) \, [e^{-\beta \phi_{ij}(r)} - 1] d\underline{r} \qquad \text{(A-10)}$$

The unlike interaction ($i \neq j$) requires estimation using the pure component interaction and we have chosen the standard mixing rule

$$T_{ij}^{*} = (T_{i}^{*}T_{j}^{*})^{1/2}$$
$$V_{ij}^{*} = \left| \frac{\overline{V_{i}^{*1/3}} + V_{j}^{*1/\overline{3}}}{2} \right|^{3} \qquad \text{(A-11)}$$

While a binary interaction may be required to account for deviations from (A-11), we have not chosen to do this.

Calculations of $y_{ij}^{hs}(r)$ for mixtures involve several facets. First, as in Chapter 4, we assume that Equation (A-9) can be adapted to calculate the hard sphere size of each of the components in the mixture. For the reduced temperature and density we chose

Table A-2

Correlation of Pure Fluid P-V-T Relations

Name	T_c, °K	V_c, $\frac{cc}{gmol}$	T^*, °K	V^*, $\frac{cc}{gmol}$	T/T^* range	ρV^* range	Max. Pr., atm.	Avg. Abs. % Error[c]
Argon-Krypton-Xenon[a]	150.7	75.44	150.7	75.44	.60-2.84	0-2.97	2800	4.13
Hydrogen	43.6[b]	51.5[b]	42.59	55.18	7.0-18.2	0-1.52	1200	0.27
Methane	190.6	99.50	187.34	99.51	.59-2.01	0-2.83	505	4.15
Nitrogen	126.3	90.1	125.27	90.80	.61-1.87	0-2.85	513	3.85
Ethane	305.4	148.0	276.22	147.25	1.13-1.85	0-2.38	680	2.14
n-Butane	425.2	255.0	424.62	256.45	.73-1.20	0-2.79	680	8.37
n-Decane	617.2	602.0	713.34	618.47	.42-.50	2.96-3.77	5103	1.06
n-Hexadecane	717.0	950.0	774.79	995.80	.38-.46	3.20-3.73	2382	1.56
Benzene	561.7	260.0	575.36	256.37	.70-.94	1.63-2.57	175	3.93
Aniline	696.8	274.0	705.93	290.53	.42-.51	3.01-3.30	987	0.51
Carbontetrachloride	556.3	276.0	530.82	282.16	.56-.64	2.69-3.13	987	1.76
Water	647.37	56.00	313.68	46.55	.95-1.14	2.50-2.68	987	0.67
Ethylene glycol	646.0	186.0	526.78	173.07	.57-.68	2.97-3.19	987	0.38

[a] Properties of krypton and xenon have been scaled using 2-parameter corresponding states (see ref. 7)

[b] Pseudocritical properties

[c] Av. Abs. % Error $\equiv \dfrac{100}{n_d} \sum\limits_{i=1}^{n_d} \left| \dfrac{p_i^{cal} - p_i^{exp}}{p_i^{exp}} \right|$

$$\tilde{T}_{ii} = T/T_i^*$$

(A-12)

$$\tilde{\rho}_{ii} = \tilde{\rho}_{mix} = \rho \sum x_i V_i^*$$

Now Equation (A-9) can be used to calculate the hard sphere diameter of each component of the (additive) hard sphere mixture.

Second, while the form of $y_{ij}^{hs}(r)$ is simple when $r < \sigma_{ij}$, the expression is much more complex for $r > \sigma_{ij}$. We have chosen to approximate $g_{ij}^{hs}(r)$ in terms of the value at contact and an equivalent pure hard sphere distribution function. An average hard sphere diameter can be defined as

$$\sigma_{av} = \sum_{i=1}^{n} x_i \sigma_i^{\alpha+1} / \sum_{i=1}^{n} x_i \sigma_i^{\alpha}$$

(A-13)

where α is some integer power to be defined later. We find $\alpha = 1$ is adequate for the present. If $g^{hs}(\sigma_{ij})$ is the contact value of the radial distribution function of the mixture and $g^{hsP}(r)$ the radial distribution function of a pure hard sphere fluid whose hard sphere diameter is σ_{av} and is at a reduced density of $\tilde{\eta} = \sum_{i=1}^{n} \rho_i \sigma_i^3$, then our approximation is

$$g_{ij}^{hs}(r) - 1 = \left| \frac{\overline{g}_{ij}(\sigma_{ij}) - \overline{1}}{\underline{g}^{hsP}(\sigma_{av}) - \underline{1}} \right| [g^{hsP}(r + \sigma_{av} - \sigma_{ij}) - 1]$$

(A-14)

The form was deduced from the results of Throop and Bearman[9] who numerically evaluated the radial distribution function for various

hard sphere binaries using the Percus-Yevick equation solution of Lebowitz.[8] The approximation should be accurate in the first shell, which makes a large fraction of the contribution to the direct correlation function integral for $r > \sigma_{ij}$.

A.3   Results

The equations presented provide a means of calculating any pair direct correlation function integral, C_{ij}, at a given temperature and set of component number densities. Thus the methods of Chapter 2 can be used to calculate the deviations of ideality of any multi-component system.

Figure A-1 shows the prediction of the deviations from ideality for the system hydrogen-benzene using the model just described and the parameters shown in Table A-2. The predicted activity coefficients are very close to the experimental data of Connolly.[10] For comparison, on the isotherm T = 533K we show fugacity that would be obtained if ideal solution had been assumed and also the predicted fugacity if the Poynting correction alone had been applied.

For other binaries the results are not quite as encouraging. Although the results at small solute concentrations are comparable to those obtained with the other model, this model predicts the onset of critical conditions at concentrations much lower than the actual (experimental) value. This does not happen with the model we are presently using. The reason is probably connected to the inability of the microscopic model to represent the critical region of the reference pure fluid.
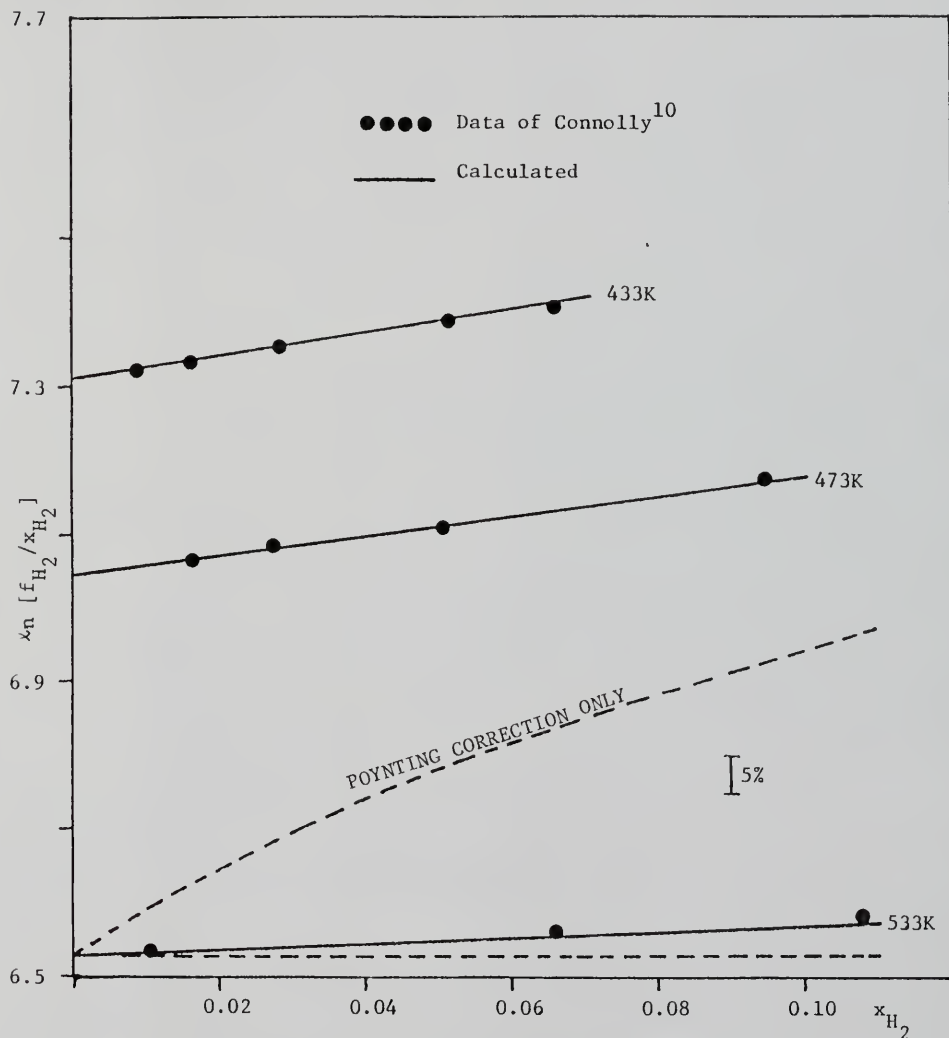
Figure A-1. Predicted nonideality of hydrogen-benzene solutions. Comparison with data of Connolly

Another problem with this model is that the expression for each pair direct correlation function integral must be integrated numerically. Thus the computer time is very large. Each calculation of a set of liquid phase activity coefficients for a binary takes about 1 second on the Amdahl computer at the University of Florida. Therefore, the calculation of an equilibrium point which necessarily involves iterations could take a prohibitive amount of computer time.

In spite of these drawbacks, which probably preclude its practical usage, this model is useful. The success obtained for the hydrogen-benzene system indicates that most of the assumptions are valid. Perhaps with minor modifications it can be made to describe properties in the critical region. Further, a model of this sort can easily be adapted to account for orientation dependent intermolecular potentials.

A.4 Computations

The integrals in Equations (A-4) and (A-10) have been evaluated by Gauss quadrature. We give here a listing of the FORTRAN subprogram that calculates the I-J direct correlation function integral of an M-component fluid at temperature TK, molar volume V and mole fraction vector $\underline{X}$. The parameters must be passed to the subroutine in the COMMON CHAR. There is no requirement on the units for the variables except that those for temperature and volume in the calling statement and the COMMON must be consistent. For completeness, we also show the subroutine

which calculates the radial distribution function of the hard sphere

fluid (GRHS) and the exponential of the Maitland and Smith pair

potential (EXBF).

References for Appendix A

1. T.M. Reed and K.E. Gubbins, "Applied Statistical Mechanics" (McGraw-Hill, New York, 1973).

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3. M. Wertheim, Phys. Rev. Lett., $\underline{8}$, 321 (1963).

4. E. Thiele, J. Chem. Phys., $\underline{39}$, 474 (1963).

5. D. Henderson and E.W. Grundke, J. Chem. Phys., $\underline{63}$, 601 (1975).

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10. J.F. Connolly, J. Chem. Phys., $\underline{36}$, 2897 (1962).

```
      SUBROUTINE DCFINT (M,I,J,C,X,V,TK)

C
C     PROGRAM TO CALCULATE THE I-J DIRECT CORRELATION FUNCTION INTEGRAL
C     OF AN M-COMPONENT FLUID AT TEMPERATURE TK, SPECIFIC VOLUME V.
C     AND SET OF MOLE FRACTIONS X USING THE MICROSCOPIC MODEL
C
C     SUBROUTINES REQUIRED : EX8F
C
C     COMMENTS :
C     * CHARACTERISTIC PARAMETERS MUST BE PASSED IN THE COMMON CHAR
C

      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /CHAR/ TSTR(10),VSTR(10)
      DIMENSION X(M),AK(6),R(10),T(200),Y(200),RSG(200),GRH(200)
      DIMENSION W(8),Z(8),WT(200),A(6)
      DATA AK/.90327658D0, 1.9153663D0,.7703880500,3.3062501D0,1.9053766
     *D-2/
      DATA Z/.0198550718D0,.1016667613D0,.23723379500D0,.4082267880D0.
     $.5917173212D0,.7627662050D0,.8983332387D0,.9801449282D0/
      DATA W/.0506142681D0,.1111905172D0,.1568533229D0,.1813418917D0,
     $.1813418917D0,.1568533229D0,.1111905172D0,.0506142681D0 /
      DATA NG/8/, NS/5/, A/0.0D0,0.04D0,0.89D0,1.0D0,1.2D0,3.0D0/
      DATA RCONV/0.4209D0/, TCONV/1.058D0/, DISP/1.11976D0/
C.....CALCULATE CHARACTERISTIC I-J PARAMETERS AND REDUCED CONDITIONS
      IF (I.NE.J) GC TO 15
      VIJ=VSTR(I)
      TIJ=TSTR(I)
      GO TO 16
   15 VIJ=(VSTR(I)**(1./3.) + VSTR(J)**(1./3.))**3/8.
      TIJ=DSQRT(TSTR(I)*TSTR(J))
   16 RR=VIJ/V*RCONV
      TR=TK/TIJ*TCONV
C.....CALCULATE RATIO OF HARD SPHERE DIAMETERS TO MIN OF I-J POTENTIAL
      VEQ=0.D0
      DO 11 K=1,M
```

```fortran
   11 VEG=VEQ+X(K)*VSTR(K)
      RHRD=VEG/V
      DO 10 K=1,M
      TS=TK/TSTR(K)
      R(K)=AK(1)/(1.DC+AK(5)*TS) + AK(2)*DEXP(-AK(3)*(RHRD+AK(4)*TS))
   10 R(K)=R(K)*(VSTR(K)/VIJ)**(1./3.)
C.... CALCULATE ZI'S AND COEFFICIENTS OF POLYNOMIAL EXPRESSION FOR THE
C     DIRECT CORRELATION FUNCTION
C     ALSO CALCULATE VOLUME FRACTION AVERAGED R - RV
      ZI1=0.0
      ZI2=0.0
      ZI3=0.0
      DO 20 K=1,M
      ZI1=ZI1 + X(K)*R(K)
      ZI2=ZI2 + X(K)*R(K)**2
   20 ZI3=ZI3 + X(K)*R(K)**3
      RV=ZI2/ZI1
      ZI0=RR*0.5236D0
      ZI1=ZI1*RR*0.5236D0
      ZI2=ZI2*RR*0.5236D0
      ZI3=ZI3*RR*0.5236D0
      IF (R(I).GT.R(J)) GO TO 21
      RI=R(I)
      RJ=R(J)
      GO TO 22
   21 RI=R(J)
      RJ=R(I)
   22 XLMDA=(RJ-RI)/2.
      RIJ=(RJ+RI)/2.
      OZI3=1.-ZI3
      AI=(9.*RI**3*ZI2**3 + OZI3*(9.*RI**2*ZI2**2 + 6.*RI**3*ZI1*ZI2 +
     1OZI3*(3.*RI*ZI2 + 3.*RI**2*ZI1 + RI**3*ZI0 + OZI3)))/OZI3**4
      BIJ=-3./2./OZI3**2*(RI*RJ*OZI3 + 2.*RIJ*ZI1 + ZI2) - 9./2./OZI3**4
     1*(2.*RI*RJ*ZI1*ZI2*OZI3 + 2.*RIJ*ZI2**2*OZI3 + 3.*RI*RJ*ZI2**3)
      D=(0.5*ZI0*OZI3**2 + 3.*ZI1*ZI2*OZI3 + 9./2.*ZI2**3)/OZI3**4
C.... CALCULATE 'C' USING GAUSS QUADRATURE
```

```fortran
      IF (IFLAG.EQ.1) GO TO 51
      DO 50 L=1,NS
      N1=(L-1)*NG
      F1=A(L+1)-A(L)
      DO 50 K=1,NG
      T(N1+K)=A(L)+F1*Z(K)
   50 WT(N1+K)=W(K)
      IFLAG=1
      N2=NG*NS
   51 DO 30 K=1,N2
      IF (T(K).GT.RIJ) GC TO 31
      Y(K)=AI
      IF (T(K).LT.XLMCA) GO TO 30
      XL=T(K)-XLMDA
      Y(K)=AI + XL**2*(BIJ + XL*D*(4.*XLMDA+XL))/T(K)
   30 CONTINUE
   31 N1=K
      DO 32 K=N1,N2
   32 RSG(K-N1+1)=(T(K)+RV-RIJ)/RV
      NP=N2-N1+1
      CALL GRHS (ZI3,NP,RSG,GRH)
      RATIO=(3./2.*RI*RJ/RIJ*ZI2 + ZI3*DZI3)/(ZI3/2.*(5.-2.*ZI3))
      DO 33 K=N1,N2
      Y(K)=(GRH(K-N1+1) - 1.0)*RATIO + 1.0
   33 CONTINUE
      XINT=0.0
      DO 60 L=1,NS
      F1=0.D0
      N1=(L-1)*NG
      DO 62 K=1,NG
      N=K+N1
   62 F1=F1 + Y(N)*(EXBF(T(N),TR) - 1.D0)*T(N)**2*WT(N)
   60 XINT=XINT + F1*(A(L+1)-A(L))
      C=12.556D0*RR*(XINT + DISP/3.D0/TR/A(NS+1)**3)
      RETURN
      END
```

```
      DOUBLE PRECISION FUNCTION EXBF(RD,TR)

C     PROGRAM CALCULATES THE EXPONENTIAL OF THE REDUCED MAITLAND AND
C     SMITH POTENTIAL AT REDUCED DISTANCE RD AND REDUCED TEMPERATURE TR
C     REFERENCE : G.C.MAITLAND AND E.B.SMITH,MOL.PHYS.,22,861(1971).

C     SUBROUTINES REQUIRED : -

      IMPLICIT REAL*8 (A-H,D-Z)
      IF (RD.LT.6.D-1) GO TO 35
      RD1=RD-1.D0
      BFE=-DEXP(-12.5D0*RD1)*(-0.29214D0+RD1*(4.41458D0+RD1*(7.70182D0
     2+RD1*(31.9293D0+RD1*(136.026D0+RD1*151.D0))))) - 1.11976D0/(RD**6+
     30.01D0) - 0.17155 1D0/(RD**8+0.01D0) - 0.013748D0/(RD**10+0.01D0)
      IF (RD.LT.2.D0) BFE=BFE+0.025D0*DEXP(-50.D0*(RD-1.33D0)**2)
      BFE=BFE/TR
      IF (BFE.LT.20.) GO TO 32
   35 EXBF =0.0
      RETURN
   32 EXBF =DEXP(-BFE)
      RETURN
      END
```

```fortran
      SUBROUTINE GRHS(ETAR,NR,RSTR,GRV)

C     PROGRAM TO CALCULATE THE RADIAL DISTRIBUTION FUNCTION OF A HARD
C     SPHERE FLUID USING THE PERCUS-YEVICK EQUATION
C     ALSO INCLUDES THE OPTION OF INCORPORATING THE EMPIRICAL CORRECTION
C     OF VERLET & WEIS
C     REFERENCES :
C     1. M.S.WERTHEIM,PHYS.REV.LETT.,10,321(1965).
C     2. L.VERLET AND J.J.WEIS, PHYS.REV.A,5,939(1972).
C
C     EXPLANATION OF PARAMETERS :
C     ETAR - REDUCED DENSITY (=PI/6*RHO*SIGMA**3)
C     NR   - NUMBER OF POINTS AT WHICH RADIAL DISTRIBUTION FUNCTION
C            IS TO BE CALCULATED
C     RSTR - VECTOR OF REDUCED DISTANCES
C     GRV  - VECTOR OF CALCULATED RADIAL DISTRIBUTION FUNCTIONS
C
C     NOTE : FOR (RSTR(I).GT.4.0) GRV(I)=1.0
C
C     IF  IVW=0      PY G(R) ONLY CALCULATED
C     IF  IVW=1      CORRECTION OF VERLET & WEIS INCORPORATED
C
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION RSTR(NR),GRV(NR)
      COMPLEX*16 T(3),TDP,C(3),P1(3),P0(3),TD,DCMPLX,CDEXP,ETFN,
     *CO(3),C1(3),C2(3)
      IVW=0
      ETA=ETAR*(1.-ETAR/16.*IVW)
      ET2=1.+ETA/2.
      F=(3.+3.*ETA-ETA**2)/(4.*ETA**2)
      XP=(DSQRT(F**2+0.125)+ F)**(1./3.)
      XM=(DSQRT(F**2+0.125)- F)**(1./3.)*(-1.0)
      TCAL=2*ETA/(1.-ETA)
      T(1)=TCAL*(-1.+XP+XM)
      T2R=TCAL*(-1.-0.5*(XP+XM))
      T2I=TCAL*0.866*(XP-XM)
```

```
      T(2)=DCMPLX(T2R,T2I)
      T(3)=DCMPLX(T2R,-T2I)
      DO 12 I=1,2
      DO 10 J=1,3
      DO 10 K=1,3
      IF (I.NE.K.AND.J.NE.K.AND.I.NE.J) GO TO 11
10    CONTINUE
11    ETFN=(1.+ETA/2.)*T(I) + (1.+2.*ETA)
      TD=2.*T(I)-T(J)-T(K)
      TDP=(T(I)-T(J))*(T(I)-T(K))
      C(I)=T(I)*ETFN/TDP
      P1(I)=T(I)*(ETFN/TDP)**2
      PO(I)=ETFN/TDP**2*(ETFN+2.*T(I)*(1.+ETA/2.) - 2.*T(I)*(2.*T(I))
     * -T(J)-T(K))*ETFN/TDP)
      C2(I)=T(I)*(ETFN/TDP)**3
      C1(I)=C2(I)/T(I)*(1. + 3.*T(I)*(1.+ETA/2.)/ETFN - 3.*T(I)*TD/TDP)
     **2.0
      CO(I)=1.5*C1(I)*(ET2/ETFN-TD/TDP) + 3.*C2(I)*(ET2/ETFN/T(I) -
     * (ET2/ETFN)**2 - (TD/T(I)+2.)/TDP + (TD/TDP)**2)
12    CONTINUE
      DO 50 IR=1,NR
      RST=RSTR(IR)
      X=RST*(ETAR/ETA)**(1./3.)
      IF (X.LE.4.) GO TO 30
      GRV(IR)=1.0
      GO TO 50
30    XGR=0.0
      XGR2=0.0
      XGR3=0.0
      IF (X.LT.1.) GO TO 22
      DO 20 I=1,2
20    XGR=XGR + C(I)*CDEXP(T(I)*(X-1.))*I
      XGR=XGR/(1.-ETA)**2
      IF (X.LT.2.) GO TO 22
      DO 21 I=1,2
21    XGR2=XGR2 + (P1(I)*(X-2.)+PO(I))*CDEXP(T(I)*(X-2.))*I
```

```
      XGR=XGR - XGR2*12.*ETA/(1.-ETA)**4
      IF (X.LT.3.) GO TO 22
      DO 24 I=1,2
   24 XGR3=XGR3 + (CO(I)+(X-3.)*(C1(I)+(X-3.)*C2(I)))*CDEXP(T(I)*(X-3.)
     * )*I
      XGR=XGR + XGR3*72.*(ETA/(1.-ETA)**3)**2
   22 GRPY=XGR/X
      IF (IVW.EQ.1) GO TO 40
      GRV(IR)=GRPY
      GO TO 50
C     CORRECTION OF PY DISTRIBUTION FUNCTION USING PRESCRIPTION OF
C     VERLET & WEIS
   40 DELG=0.0
      ABD=0.75*ETA**2*(1.-ETA*(0.7117+0.114*ETA))/(1.-ETA)**4
      URD=24.*ABD*(1.-ETA)**2/ETA/(1.+ETA/2)*(RST-1.)
      IF (DABS(URD).GT.10.0) GO TO 60
      DELG=ABD/RST*DEXP(-URD)*DCOS(URD)
   60 GRV(IR)=GRPY+DELG
   50 CONTINUE
      RETURN
      END
```

CARNAHAN–STARLING EQUATION FOR MIXTURES

The Carnahan–Starling[1,2] equation provides a very accurate expression for the calculation of the properties of hard sphere mixtures. From this equation the i-j direct correlation function of an n-component hard sphere mixture of component number densities $\rho_1, \rho_2 \ldots, \rho_n$ and hard sphere sizes $\sigma_1, \sigma_2, \ldots \sigma_n$ can be expressed as

$$
-\frac{C_{ij}}{\xi_0} = (\sigma_i + \sigma_j)^3/(1-\xi_3) + \Big\{ 3\sigma_i\sigma_j\xi_2[(\sigma_i + \sigma_j)^2 + \sigma_i\sigma_j] + 3\xi_1(\sigma_i\sigma_j)^2(\sigma_i + \sigma_j)
$$

$$
+ \xi_0(\sigma_i\sigma_j)^3/(1-\xi_3)^3 + 9(\sigma_i\sigma_j\xi_2)^3/(1-\xi_3)^3 + \xi_2(\sigma_i\sigma_j)^2/(1-\xi_3)^3
$$

$$
\times \{9\xi_2(\sigma_i + \sigma_j) + 6\xi_1\sigma_i\sigma_j + [6 + \xi_3(-15 + 9\xi_3)]/\xi_3
$$

$$
- (\sigma_i + \sigma_j)\,\xi_2[6 + \xi_3(-15 + 12\xi_3)]/\xi_3^2
$$

$$
+ \xi_2^2\sigma_i\sigma_j[6 + \xi_3(-21 + \xi_3(26 - 14\xi_3))]/\xi_3^3 \}
$$

$$
+ 6\xi_2(\sigma_i\sigma_j)^2 \,\ell n(1-\xi_3)/\xi_3^3 \,\{1 - (\sigma_i + \sigma_j)\xi_2 + \xi_2^2\sigma_i\sigma_j/\xi_3\}
$$

where

$$
\xi_\alpha = \frac{\pi}{6} \sum_{i=1}^{n} \rho_i\sigma_i^\alpha
$$

In the limiting case of a pure fluid, the above equation reduces to

$$
- C = 2\xi_3(4 - \xi_3)/(1-\xi_3)^4
$$

References for Appendix B

1. N.F. Carnahan and K.E. Starling, J. Chem. Phys., 51, 635 (1969).

2. G.A. Mansoori, N.F. Carnahan, K.E. Starling and T.W. Leyland, J. Chem. Phys., 54, 1523 (1971).

APPENDIX Ç

This appendix describes the numerical method we use to calculate the activity coefficients of the components in an arbitrary n-component system due to a change from a reference state to a final state.

The critical state must be specified by the temperature T, the set of mole fractions $\underline{x}^r$, the molar volume v^r, and the pressure P^r. The final state can be specified by the same temperature T (note that the theory describes only isothermal changes), the set of final mole fractions $\underline{x}^f$, and either the final pressure P^f or the final molar volume v^f. With the former specification, Equation (2-22) must first be used to solve for v^f and then Equation (2-25) can be used to calculate the activity coefficients; the latter specification allows direct evaluation of the activity coefficients from Equation (2-25).

ACTCF is a subroutine which implements the above scheme. All integrations are done by an 4-point Gauss quadrature.[1] The direct correlation function integrals at any given condition are calculated by the subroutine DCFINT. The evaluation of v^f requires an approximate solution. This is accomplished by using the subroutine NONLN3.

Since the solution for v^f is approximate, an initial guess is required. This guess does not have to be very accurate and thus for this purpose we have adapted the correlation of Prausnitz and Chueh[2] for the saturated volume of a multicomponent liquid. The estimate assumes that the change in volume from the initial to final state

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follows their two-parameter corresponding states theory with the critical constants replaced by our characteristic parameters.

$$(v^f)^{\text{initial guess}} = v^r + (v^f - v^r)^{\text{Prausnitz-Chueh}} \qquad \text{(C-1)}$$

This initial guess is apparently adequate since we have not experienced any convergence problems for any system.

We give a listing of the subroutine ACTCF, GDFINT, NONLN3 and of two sample programs which demonstrate how ACTCF is used.[*]

References for Appendix C

1. M. Abramowitz and I.A. Stegun, "Handbook of Mathematical Functions" (Dover Publications, Inc., New York, New York, 1965).

2. J.M. Prausnitz and P.L. Chueh, "Computer Calculations for High-Pressure Vapor-Liquid Equilibria" (Prentice-Hall, Inc., Englewood Cliffs, NJ, 1968).

---

[*] Note that all computations are done in double precision since this is required by the nonlinear fitting subroutine.

```
      SAMPLE PROGRAMS

C
C.....  1. SAMPLE PROGRAM FOR THE CALCULATION OF THE ACTIVITY COEFFICIENTS
C       OF A BINARY GAS-SOLVENT SYSTEM AT PRESSURE P AND MOLE FRACTION X1
C       LET THE REFERENCE STATE BE THE SATURATED SOLVENT
C       DENOTE THE GAS AS COMPONENT 1
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION XS(2),XF(2),GAMMA(2)
        DATA XS/0.D0,1.D0/
        COMMON /CHAR/ TSTR(10),VSTR(10),XKIJ(10,10)
C       READ CHARACTERISTIC PARAMETERS
        READ (5,N1) (TSTR(I),VSTR(I),I=1,2),XKIJ(1,2)
C       READ DATA
        READ (5,N1) T,PSAT2,VSAT2,P,X1
        XF(1)=X1
        XF(2)=1.D0-X1
        CALL ACTCF (2,T,XS,VSAT2,PSAT2,XF,P,VF,GAMMA,ICMPR,1)
C       SUBROUTINE ACTCF CALCULATES THE ACTIVITY COEFFICIENTS (GAMMA),
C       ANC SPECIFIC VOLUME (VF)
          .
          .
C.....  2. SAMPLE PROGRAM FOR THE CALCULATION OF HENRY'S CONSTANT OF A GAS
C       (CCMPONENT 1) IN SCLVENT3 GIVEN HENRY'S CONSTANT OF THE GAS IN
C       SOLVENT2
        IMPLICIT REAL*8 (A-H,O-Z)
        DIMENSION XS(3),XF(3),GAMMA(3)
        COMMON /CHAR/ TSTR(10),VSTR(10),XKIJ(10,10)
        DATA XS/0.D0,1.D0,0.D0/, XF/0.D0,0.D0,1.D0/
C       READ CHARACTERISTIC PARAMETERS; NOTE THAT THIS CALCULATION IS
C       INDEPENDANT OF XKIJ(2,3)
        READ (5,N1) (TSTR(I),VSTR(I),I=1,3),XKIJ(1,3),XKIJ(1,2),XKIJ(1,3)
C       READ DATA; NOTE THAT THIS CALCULATION DOES NOT USE THE PRESSURE
        READ (5,N1) T,VSAT2,VSAT3,H12
        CALL ACTCF (3,T,XS,VSAT2,P,XF,P,VSAT3,GAMMA,ICMPR,0)
        H13=H12*GAMMA(1)
          .
          .
```

```
      SUBROUTINE ACTCF (N,T,XS,VS,PS,XF,P,VF,GAMMA,ICMPR,IVCAL)

C     PROGRAM TO CALCULATE ACTIVITY COEFFICIENTS OF AN N-COMPONENT
C     SYSTEM AT TEMPERATURE T FOR A CHANGE FROM THE INITIAL STATE TO
C     THE FINAL STATE
C
C     EXPLANATION OF PARAMETERS :
C
C     N      - NUMBER OF COMPONENTS
C     T      - TEMPERATURE, K
C     XS     - VECTOR OF MOLE FRACTIONS OF INITIAL STATE
C     VS     - SPECIFIC VOLUME OF INITIAL STATE, CC/GMOL
C     PS     - PRESSURE OF INITIAL STATE, ATM
C     XF     - VECTOR OF MOLE FRACTIONS OF FINAL STATE
C     P      - PRESSURE OF FINAL STATE, ATM
C     VF     - SPECIFIC VOLUME OF FINAL STATE, CC/GMOL
C     GAMMA  - VECTOR OF CALCULATED ACTIVITY COEFFICIENTS
C     ICMPR  - PARAMETER WHICH INDICATES IF NEGATIVE COMPRESSIBILITY
C              WAS ENCOUNTERED IN INTEGRATION PATH
C              ICMPR=0 : NO NEGATIVE COMPRESSIBILITY
C              ICMPR=1 : NEGATIVE COMPRESSIBILITY ENCOUNTERED
C     IVCAL  - PARAMETER WHICH INDICATES WHETHER FINAL STATE VOLUME OR
C              PRESSURE IS SPECIFIED
C              IVCAL=1 : PRESSURE SPECIFIED
C              IVCAL=0 : VOLUME SPECIFIED
C
C     SUBROUTINES REQUIRED : DCFINT,NONLN3
C
C     COMMENTS :
C     * THE CHARACTERISTIC PARAMETERS ARE PASSED TO THE PROGRAM IN THE
C     IN THE COMMON CHAR
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Z(8),W(8),XS(N),RSI(10),XF(N),RFI(10),XM(10),RDI(10),
     * GAMMA(N),C(10,10,8)
      COMMON /CHAR/ TSTR(10),VSTR(10),XKIJ(10,10)
      COMMON /CONV/ ERR
```

```
      DATA Z/.069431844200,.330009478200,.699990521800,.930568155800/
      DATA W/.173927422600,.173927422600,.326072577400,.326072577400/
      DATA NG/4/,THRD/.333333330/
      VFUN(TR)=TR*(.951300-2+TR*(.2109100-6.9220-2*TR)) + 7.480-2/TR
     *  - 8.447600-2*DLOG(1.00-TR)
      ICMPR=0
      RT=82.05*T
      RS=1.DO/VS
      DO 60 I=1,N
   60 RSI(I)=XS(I)*RS
      IF (IVCAL.EQ.0) GO TO 27
C.....INITIAL GUESS FOR MIXTURE VOLUME
      VSTS=0.DO
      VSTF=0.DO
      TSTS=0.DO
      TSTF=0.DO
      DO 50 I=1,N
      VSTS=VSTS+XS(I)*VSTR(I)
      VSTF=VSTF+XF(I)*VSTR(I)
      FP=VSTR(I)**2*TSTR(I)
      TSTS=TSTS+XS(I)**2*FP
      TSTF=TSTF+XF(I)**2*FP
      IF (I.EQ.N) GO TO 51
      II=I+1
      DO 50 J=II,N
      FP=16.DO*VSTR(I)*VSTR(J)*DSQRT(TSTR(I)*TSTR(J)*TSTR(J)*VSTR(I)*VSTR(J))/
     *(VSTR(I)**THRD+VSTR(J)**THRD)**3
      TSTS=TSTS+XS(I)*XS(J)*FP
   50 TSTF=TSTF+XF(I)*XF(J)*FP
   51 TRS=T/TSTS*VSTS**2
      IF (TRS.GE..995DO) TRS=.995DO
      TRF=T/TSTF*VSTF**2
      IF (TRF.GE..995DO) TRF=.995DO
      VF=VSTF*(VS/VSTS + VFUN(TRF) - VFUN(TRS))
C.....CALCULATION OF MIXTURE VOLUME
   27 RG=1.D3/VF
```

```
      RX=0.D0
      ITEST=2
      IF (IVCAL.EQ.0) GO TO 26
 20   CALL NONLN3 (ITEST,RX,ERR,5.D-1,1.D-3,1.D-1,1.D-10)
      GO TO (21,21,23,24), ITEST
 21   IF (ITEST.EQ.2.AND.RX.EQ.RXOLD) GO TO 22
      IF ((RX+RG).GT.0.D0) GO TO 26
      ERR=10.*P
      GO TO 20
 26   CONTINUE
      RF=(RG+RX)*1.D-3
      VF=1.D0/RF
      RD=RF-RS
      DO 30 I=1,N
      RFI(I)=XF(I)*RF
 30   RDI(I)=RFI(I)-RSI(I)
      XNT=0.D0
      DO 31 K=1,NG
      VK=1.D0/(RS+Z(K)*RD)
      DO 33 I=1,N
 33   XM(I)=(RSI(I)+Z(K)*RDI(I))*VK
      CMPR=0.D0
      IENTRY=0
      DO 34 I=1,N
      DO 34 J=1,N
      CALL DCFINT(N,I,J,C(I,J,K),XM,VK,T,IENTRY)
      IENTRY=1
      FACT=1.
      IF (I.NE.J) FACT=2.
      CMPR=CMPR+XM(I)*XM(J)*C(I,J,K)*FACT
 34   C(J,I,K)=C(I,J,K)
      IF (CMPR.GT.1.D0.AND.ITEST.EQ.2) ICMPR=1
      XNTK=0.D0
      DO 35 I=1,N
      XNTI=0.D0
      DO 36 J=1,N
```

```fortran
   36 XNTI=XNTI+XM(J)*C(I,J,K)
   35 XNTK=XNTK+RDI(I)*(1.D0-XNTI)
   31 XNT=XNT+XNTK*W(K)
      P2=PS+XNT*RT
      ERR=P2-P
      RXOLD=RX
      IF (ITEST.EQ.2) GO TO 22
      GO TO 20
   23 WRITE (6.110) P,P2,ERR,VF
  110 FORMAT (' ERROR IN VOLUME CALCULATIONS',4F12.4,'  -ACTCF')
      GO TO 22
   24 WRITE (6.111) P,P2,ERR,VF
  111 FORMAT (' ROUNDOFF ERR IN VOL CALC',4F12.4,'  -ACTCF')
   22 CONTINUE
C.... CALCULATION OF ACTIVITY COEFFICIENTS
      DO 45 I=1,N
      XNT=0.D0
      DO 41 K=1,NG
      VK=1.D0/(RS+Z(K)*RD)
      XNTJ=0.D0
      DO 44 J=1,N
   44 XNTJ=XNTJ+RDI(J)*C(I,J,K)
   41 XNT=XNT+XNTJ*VK*W(K)
   45 GAMMA(I)=DEXP(-XNT)*RF/RS
      RETURN
      END
```

```
      SUBROUTINE DCFINT (M,I,J,C,X,V,T,IENTRY)

C     PROGRAM CALCULATES THE I-J DIRECT CORRELATION FUNCTION INTEGRAL
C     OF A M-COMPONENT MIXTURE
C
C     EXPLANATION OF PARAMETERS :
C     M      - NUMBER OF COMPONENTS
C     I,J    - I-J PAIR FOR WHICH DCF INTEGRAL IS TO BE CALCULATED
C     C      - CALCULATED VALUE OF THE I-J DCF INTEGRAL
C     X      - VECTOR OF MOLE FRACTIONS
C     V      - SPECIFIC VOLUME, CC/GMOL
C     T      - TEMPERATURE, K
C     IENTRY - PARAMETER TO SAVE COMPUTER TIME
C              IENTRY=0  FIRST ENTRY AT GIVEN CONDITIONS
C              IENTRY=1  SUBSEQUENT ENTRIES AT SAME CONDITIONS
C
C     SUBROUTINES REQUIRED : -
C
C     COMMENTS :
C     * THE CHARACTERISTIC PARAMETERS ARE PASSED TO THE SUBROUTINE IN
C       THE COMMON CHAR
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /CHAR/ TSTR(10),VSTR(10),XKIJ(10,10),R(10)
      DIMENSION X(M),A(15),R(10)
      DATA A/.54008832D0,.12669802D1,.5123547D-1,.2910742421D1,.25167259
     *D1,.21595955D1,.6426952D0,.1756588D0,.1887482D0,.1795233D2,
     *.481971D0,.766960099D0,.766313D0,.809657804D0,.240628663D0/
      DATA THRD/.333333333D0/
      IF (IENTRY.EQ.1) GO TO 21
C.... CALCULATION OF HARD SPHERE DIAMETERS
      VEQ=X(M)**2*VSTR(M)
      IF (M.EQ.1) GO TO 12
      M1=M-1
      DO 11 K=1,M1
      VEQ=VEQ+X(K)**2*VSTR(K)
```

```
      L1=K+1
      DO 11 L=L1,M
      VSKL=(VSTR(K)**THRD+VSTR(L)**THRD)**3/8.D0
   11 VEQ=VEQ+2.D0*X(K)*X(L)*VSKL
   12 RR=VEQ/V
      DO 10 K=1,M
      TR=T/TSTR(K)
      F =A(7)/TR**A(8)
      IF (TR.LT..73D0)F=A(14)/DEXP(A(15)*TR)
      TPR=RR+A(1)*TR
      IF (TPR.GT.5.D0) GO TO 10
      F= F + A(2)/DEXP(A(4)*TPR**2) - A(3)/DEXP(A(5)*(TPR-A(6))**2)
      EXPNT=A(10)*((TR-A(13))**2+A(11)*(RR-A(12))**2)
      IF (EXPNT.LT.10.D0) F=F+ A(9)/DEXP(EXPNT)
   10 R(K)=(F*VSTR(K)/2.0944D0)**THRD
C.... CALCULATION OF HARD SPHERE DIRECT CORRELATION FUNCTION INTEGRAL
C     FROM CARNAHAN-STARLING EQUATION
      ZI1=0.D0
      ZI2=0.D0
      ZI3=0.D0
      DO20 K=1,M
      ZI1=ZI1+X(K)*R(K)
      ZI2=ZI2+X(K)*R(K)**2
   20 ZI3=ZI3+X(K)*R(K)**3
      ZI0=.5236D0/V
      ZI1=ZI1*ZI0
      ZI2=ZI2*ZI0
      ZI3=ZI3*ZI0
      OZI3=1.D0-ZI3
   21 RIJA=R(I)+R(J)
      RIJP=R(I)*R(J)
      CHS=RIJA**3/OZI3 + (3.D0*RIJP*ZI2*(RIJA**2+RIJP) + 3.D0*ZI1*RIJP
     1**2*RIJA + ZI0*RIJP**3)/OZI3**2 + 3.D0*ZI2*RIJP**2*(3.D0*ZI2*RIJA
     2+2.D0*ZI1*RIJP)/OZI3**3 + 9.D0*(RIJP*ZI2)**3/OZI3**4 +
     3ZI2*RIJP**2*((6.D0+ZI3*(-15.D0+9.D0*ZI3))/OZI3**3/ZI3 + 6.D0*DLOG(
     40ZI3)/ZI3**2-RIJA*ZI2*((6.D0*ZI3*(-15.D0+12.D0*ZI3))/(OZI3*ZI3))
```

```fortran
     5**2/OZI3 + 6.D0*DLOG(OZI3)/ZI3**3) + ZI2**2*RIJP*((6.D0+ZI3*(-21.
     6D0+ZI3*(26.D0-14.D0*ZI3)))/(OZI3*ZI3)**3/OZI3+ 6.D0*DLOG(OZI3)/
     7ZI3**4))
      CHS=-CHS*ZIO
C.... CALCULATION OF SECOND VIRIAL COEFFICIENT
      VSIJ=VSTR(I)
      IF (I.NE.J) VSIJ=(VSTR(I)**THRD+VSTR(J)**THRD)**3/8.D0
      TRI=TSTR(I)/T
      IF (I.NE.J) TRI=DSQRT(TSTR(I)*TSTR(J))*(1.D0-XKIJ(I.J))/T
      IF (TRI.GT..3125D0) GO TO 40
      B2RF=(.3301D0-TRI*(.1376D0+TRI*1.972D0))*VSIJ/V
      GO TO 41
   40 B2RF=(.4966D0-TRI*(1.1340D0+TRI*(.4759D0+TRI*(.0415D0+TRI**5*
     *.00209D0))))*VSIJ/V
C.... CALCULATION OF DIRECT CORRELATION FUNCTION INTEGRAL
   41 B2HS=.2618D0*(R(I)+R(J))**3/V
      C=CHS-2.D0*(B2RF-B2HS)
      RETURN
      END
```

```
C      SUBROUTINE NONLN3 (ITEST,X,FX,XSTEP,DX,DF,MAXFUN)
C
C      SUBROUTINE SOLVES THE EQN FX(X)=0
C
C      EXPLANATION OF PARAMETERS :
C      ITEST  - PARAMETER WHICH CONTROLS SOLUTION PROCEDURE (SEE COMMENT)
C      X      - INDEPENDANT VARIABLE; ON ENTRY CONTAINS INITIAL GUESS
C               OF ROOT
C      FX     - DEPENDANT VARIABLE WHOSE ZERO IS TO BE FOUND
C      XSTEP  - STEP SIZE OF INITIAL SEARCH
C      DX,DF  - CONVERGENCE CRITERIA
C               IF THERE IS A ZERO CONVERGENCE IS ASSUMED IF :
C               (DABS(DEL).LT.DX.AND.DABS(FX).LT.DF)
C               IF THE PROGRAM DETERMINES THERE IS NO ZERO CONVERGENCE
C               IS ASSUMED IF :
C               (DABS(DEL).LT.DX.OR.DABS(FX).LT.DF)
C               DEL = DIFFERENCE BETWEEN BEST VALUE OF X AND NEXT
C                     ESTIMATE OF ZERO
C      MAXFUN - MAXIMUM NUMBER OF FUNCTION EVALUATIONS
C
C      SUBROUTINES REQUIRED : -
C
C      COMMENTS :
C      SUBROUTINE FITS A QUADRATIC TO THE BEST THREE POINTS
C      AND THEN EXTRAPOLATES TO ZERO. IF THE FITTED QUADRATIC HAS NO ZERO
C      THE PROGRAM EXTRAPOLATES TO THE MINIMUM
C
C      RECOMMENDED USAGE :
C      ITEST=2
C   10 CALL NONLN3 (ITEST,X,FX,XSTEP,DX,DF,MAXFUN)
C      GO TO (11,12,13,14),ITEST
C   11 EVALUATE FX AT X; GO TO 10
C   12 NORMAL EXIT; CONVERGENCE ACHIEVED
C   13 ERROR EXIT; 'MAXFUN' FUNCTION EVALUATIONS EXCEEDED
C   14 ERROR EXIT; ROUND-OFF ERROR
C
```

```
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(3),F(3)
C.....  INITIAL EVALUATIONS OF FX AT X AND X +/- XSTEP
      IF (ITEST.NE.2) GO TO 10
      NITER=2
      ITEST=1
      Y(1)=X
      J=3
      NUM=1
      RETURN
 10   GO TO (11,12,13),NUM
 11   Y(2)=X+XSTEP
      X=Y(2)
      F(1)=FX
      NUM=2
      RETURN
 12   Y(3)=Y(2)-2.D0*XSTEP
      X=Y(3)
      F(2)=FX
      NUM=3
      RETURN
C.....  FINDING BEST AND WORST POINTS
 13   F(J)=FX
      I=1
      J=1
      DO 14 K=2,3
      IF (DABS(F(K)).LT.DABS(F(I))) I=K
      IF (DABS(F(K)).GT.DABS(F(J))) J=K
 14   CONTINUE
C.....  CALCULATING NEXT GUESS BY EXTRAPOLATING QUADRATIC TO ZERO
      DNOM=(Y(1)-Y(2))*(Y(2)-Y(3))*(Y(3)-Y(1))
      IF (DNOM.NE.0.D0) GO TO 42
      ITEST=4
      RETURN
 42   A1=((F(1)-F(2))*(Y(1)**2-Y(3)**2) - (F(1)-F(3))*(Y(1)**2-Y(2)**2)
     *)/DNOM
```
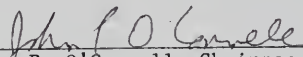
```fortran
      A2=((F(1)-F(3))*(Y(1)-Y(2))- (F(1)-F(2))*(Y(1)-Y(3))/(Y(1)-Y(3))/DEN)
      C1=A1+2.D0*A2*Y(I)
      C2=A2*2.D0
      IF (C2.NE.0.D0) GO TO 43
      DEL=-C1/F(I)
      GO TO 41
   43 FUN=C1**2-2.D0*F(I)*C2
      IF (FUN.LT.0.D0) GO TO 40
      D1=-C1/C2
      D2=DSQRT(FUN)/C2
      DEL=D1+D2
      IF (DABS(DEL).GT.DABS(D1-D2)) DEL=D1-D2
      GO TO 41
   40 DEL=-C1/C2
   41 X=Y(I)+DEL
      Y(J)=X
C.....RETURN WITH ESTIMATE OF ROOT IF CONVERGENCE CRITERION IS MET
      IF (FUN.LT.0.D0) GO TO 20
      IF (DABS(DEL).LT.DX.AND.DABS(F(I)).LT.DF) ITEST=2
      GO TO 21
   20 IF (DABS(DEL).LT.DX.OR.DABS(F(I)).LT.DF) ITEST=2
   21 IF (ITEST.EQ.2) RETURN
C.....ERROR RETURN IF NUMBER OF FUNCTION EVALUATIONS EXCEEDS MAXFUN
      NITER=NITER+1
      IF (NITER.GT.MAXFUN) ITEST=3
      RETURN
      END
```

BIOGRAPHICAL SKETCH

Paul Mathias was born on November 11, 1952, in Bangalore, India. He graduated from St. Joseph's B.H. School in 1968 and received his Bachelor of Technology in Chemical Engineering from I.I.T., Madras, in 1974. He commenced graduate studies in the Department of Chemical Engineering, University of Florida, in September 1974, and received the Master of Science degree in December, 1975.
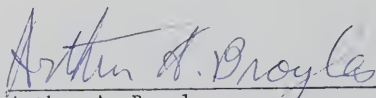
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John P. O'Connell, Chairman
Professor of Chemical Engineering

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Dinesh O. Shah
Professor of Chemical Engineering and
Anesthesiology

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Arthur A. Broyles
Professor of Physics

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June, 1978

Dean, College of Engineering

Dean, Graduate School